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Radio Frequency Enhanced Decontamination of Soils Contaminated with Halogenated Hydrocarbons

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RADIO FREQUENCY ENHANCED DECONTAMINATION OF SOILS CONTAMINATED WITH HALOGENATED HYDROCARBONS

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16. ABSTRACT

There has been considerable effort in the development of innovative treatment technologies for the clean up of sites containing hazardous wastes such as hydrocarbons and chlorinated hydrocarbons. Typical examples of such waste material are: chlorinated solvents, polychlorinated biphenyls, waste aviation fuels, gasoline, etc. The feasibility of treating waste sites containing such materials by in-situ radio frequency heating was established by this study through bench- and pilot-scale experiments. A design for an in-situ field test was developed for the treatment of sites containing solvents and aviation fuel. Cost studies were performed to estimate the treatment cost of a system for the decontamination of sites containing fuels, etc.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

Considerable effort has been spent in the development of innovative treatment technologies for the clean up of sites containing hazardous wastes such as hydrocarbons and chlorinated hydrocarbons. Typical examples of such waste material are: chlorinated solvents, polychlorinated biphenyls, waste aviation fuels, gasoline, etc. The feasibility of treating waste sites containing such materials by in-situ radio frequency heating was established by this study through bench- and pilot-scale experiments. A design for an in-situ field test was developed for the treatment of sites containing solvents and aviation fuel. Cost studies were performed to estimate the treatment cost of a system for the decontamination of sites containing fuels, etc.

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SUMMARY AND RECOMMENDATIONS

INTRODUCTION

The feasibility of the radio frequency (RF) in situ heating and soil decontamination process was successfully established in this project. In a related but different project funded by U.S. Air Force, a successful field test has been conducted in which 500 cu ft of soil containing jet fuel and chlorinated solvents was decontaminated by in situ heating. The results of these two studies warrant further optimization and scale up of the process.

In this project, feasibility of the following was established:

- sandy soil containing jet fuel and chlorinated solvents can be decontaminated by heating to 88° to 160° C for a period of 14 to 40 hrs.
- 90 to 99% decontamination of fuels and solvents was achieved.
- Aroclor 1242 can be removed from sandy soil by heating to a temperature range of 150° to 300°C.
- 72 to 99% removal was obtained for Aroclor 1242 depending on the treatment conditions.
- In the above experiments vaporization, steam distillation or stripping is used as the decontamination mechanism.
- The vaporized contaminants are recovered as a high concentration gas mixture from the soil surface. Steam is also present from soil moisture. This gas stream will require on site treatment.
- Chemical decontamination of Aroclor 1260 with the in situ application of potassium polyethylene glycolates followed by in situ heating does not appear to be feasible.

- Feasibility of the in situ heating process should be evaluated for polar materials, and for different types of soil.

DECONTAMINATION OF SOIL CONTAINING FUELS AND SOLVENTS

Bench and pilot scale experiments were performed on 75 to 4000 g of spiked soil containing tetrachloroethylene and chlorobenzene. In these experiments 90 to 99 percent removal of the contaminants was observed. The initial contaminant concentration level ranged between 0.5 to 1000 ppm. Mass balance calculations were done for the bench scale experiments. Mass balance closure of 75 to 104% percent was demonstrated in most of the experiments. The pilot scale experiments were performed on 6-ft tall columns of soil. It was shown that uniform decontamination occurs along the length of the soil bed.

Jet fuel contaminated soil was heated in 6-ft tall columns. It was shown that 90 to 99% removal of total aromatics and total non-aromatic fraction is feasible by treatment at 150° to 160°C for a period of 14 to 40 hrs.

IN SITU FIELD TEST

A field test design was prepared for heating 500 cu ft of soil containing solvents and jet fuel. An in situ field test has been conducted under a separate project funded by U.S. Air Force, Headquarters, Air Force Engineering and Service Center, Tyndall Air Force Base, Florida. Preliminary results of this in situ test indicate 94 and 99% removal of total aliphatics and total aromatics, respectively.

THERMAL DECONTAMINATION OF AROCLOR 1242

Soil spiked with Aroclor 1242 was heated to a temperature range of 150° to 300°C. 72 to 99% removal of PCB was observed depending on the temperature. It was discovered that mass balance closure on Aroclor 1242 is inversely related to the treatment temperature. For example, at 300°C, 99% removal of Aroclor 1242 was observed but the mass balance closure was only 7 to 17%. On the other hand, at 150°C, 72 to 87% removal and a mass balance closure of 73 to 82% was observed. In these experiments Soxhlet extraction of soil was utilized to determine PCB concentration in soil. Further work is necessary to determine the fate of PCB in those experiments where good removal but poor mass balance was obtained.

CHEMICAL DECONTAMINATION OF AROCLOR 1260

The feasibility of in situ chemical treatment of Aroclor 1260 with potassium polyethylene glycolate (KPEG) was investigated. The RF in situ heating technique is used to promote the reaction by removing the moisture and increasing the reaction rate at higher temperature.

When the soil is well mixed with KPEG and heated in a loosely covered container in an oven at 140°C, up to 99% destruction of Aroclor 1260 is obtained in 2.5 to 8 hr. When a soil column containing Aroclor 1260 and KPEG is heated to 60°-140°C in a cylindrical reactor, only 16 to 35% destruction of Aroclor 1260 was observed. Additional experiments are necessary to determine whether air is necessary to support the reaction between KPEG and Aroclor 1260-containing soil. The preliminary conclusion, however is that in situ treatment of soil containing Aroclor 1260 with KPEG reagent and RF heating may not be feasible.

COST FOR TREATMENT OF FUELS AND SOLVENTS

Treatment cost for soil containing jet fuel and chlorinated solvents was developed for 74,000 cu. ft (96 ft x 96 ft x 8 ft) of soil. The capital cost of the RF treatment system is estimated to be $1.6 million. The total treatment cost per 100 lb varies between $1.50 to $2.90 depending on the soil moisture content (5 to 20%) and treatment temperature (100° to 250°C).

DESCRIPTION AND ADVANTAGES OF THE HEATING SYSTEM

In situ RF heating is performed by energizing the soil with electromagnetic energy in the radio frequency band. The heating mechanism is similar to that of a microwave oven. The energy is deposited by means of an electrode array emplaced in bore holes drilled through the soil. The array is covered by a vapor barrier for the containment and collection of gases and vapors rising to the surface.

The frequency of the applied power is selected from the industrial, scientific and medical (ISM) band set aside by the Federal Communications Commission. The specific frequency is selected based on the dielectric properties of the soil, the depth of treatment and the size of the heated volume.

The main advantages of RF heating are: true in situ process is feasible, heat transfer fluids or fuel combustion products do not dilute the gases and vapors, heating is not dependent on relatively slow processes of conduction or convection, and the process is cost effective.

RECOMMENDATIONS

It is recommended that the feasibility of thermal recovery of fuels, solvents and lower chlorinated PCB's be extended to other types of soils such as clay and loam . All the thermal recovery experiments performed in this project were done with sandy soil.

Other types of chemical contaminants should be evaluated for decontamination by the thermal method. Specifically polar materials which are likely to exhibit stronger adsorption characteristics should be evaluated for each of the three different soil types. For example, materials like phenols, amines, organic acids etc. should be studied. Different types of other chemicals may be amenable to decontamination by the in situ heating methods. For example, pesticides and other agricultural chemicals, and coal derived liquids present as contaminants at the sites of old coal-gas plants should be evaluated in laboratory studies.

Through a simple modification of the heating system it should be possible to treat contaminated soil surrounding leaking underground storage tanks. Feasibility studies should be conducted on this concept.

It was shown that significant reduction of Aroclor 1242 concentration in soil can be achieved by thermal treatment of PCB-contaminated soil. However, problems were encountered in closing a mass balance on PCB. Additional studies should be performed to determine the fate of the PCB molecule when soil is heated to a temperature range of 150°-300°C.

In situ chemical decontamination of soil by the application of KPEG reagent should be further studied to evaluate the effects, if any, of reaction atmosphere. Experiments on soil decontamination should be performed under nitrogen as well as under different compositions of nitrogen/oxygen blends.

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SECTION 1

INTRODUCTION

Each year, various agencies of the U.S. Government and institutions in the private sector discover new locations of previously forgotten waste disposal sites which pose a continuous threat to the environment, public safety and health. Such sites pose a threat because they contain hazardous chemical substances which were disposed of improperly in uncontrolled burial sites or due to failure of controlled sites to prevent migration of mobile chemicals. Two large families of hazardous chemicals of commerce which were disposed in such sites as waste are hydrocarbons and chlorinated hydrocarbons.

Over the last 50 to 80 years, millions of tons of such chemicals have been disposed of by this and other environmentally unsound methods. For many chemicals, their hazardous and toxic properties were not known at the time of disposal and, therefore, burial in uncontrolled landfills was considered appropriate. For example, polychlorinated biphenyls, DDT, hexchlorobenzene, pentachlorophenol, creosote, etc., were large-volume chemicals that were routinely produced, used and disposed of until their harmful effects on the environment were understood. Although many such chemicals are now banned from commercial use or have strict use limitations, they persist in the environment due to their chemical stability. They are also wide-spread,[1] having escaped from their original sites of disposal due to fluid mobility, leaching action of rain, and airborne dispersion as vapor and aerosol emissions from the disposal sites.

Clean-up of soils contaminated by uncontrolled landfills and hazardous waste spills can be both expensive and technically challenging. Many hazardous chlorinated hydrocarbons are extremely stable and cannot be adequately rendered harmless by well known treatment methods such as chlorolysis, catalytic dehydrogenation, molten salt reactions, and ozone treatment.[2] Because the concentrations of the hazardous chemicals found in soil are low, mass transfer and reaction rates tend to be low also, requiring large processing equipment.

Conventional soil clean-up technologies require excavation of the soil prior to its treatment. Excavation is expensive and poses an increased risk of exposure and further dispersion of the contaminants during material handling steps. On the other hand, in-situ treatment processes offer inherent advantages such as:

- reduced emissions
- on-site treatment
- expensive reactors are unnecessary
- Long residence time can be economically provided, thus less drastic temperature and pressure conditions can be economically justified.
- In certain situations, delisting will not be necessary or delisting requirements will be relaxed.

Radio frequency (RF) in-situ heating is a novel technique which can provide uniform decontamination by heating large volumes of soil formations uniformly and rapidly to a temperature range of 100°-400°C. Several related in-situ treatment processes can be devised based on this technology. In this project, the feasibility of two different in-situ heating processes was evaluated through bench- and pilot-scale experiments. The two processes are:

- in-situ thermal treatment of soils containing solvents, fuels, PCB's, etc.
- in-situ chemical treatment of soils containing PCB's.

The following types of experiments were performed to show the feasibility of a thermal desorption/evaporation process for in-situ decontamination of soils.

- 75-gm of sandy soil containing tetrachloroethylene (TRCE), chlorobenzene (CBZ) was 90-99% decontaminated at 88°-160°C in a time of 3.5 to 4.0 hours (Section 3)

- 6-ft tall columns of sandy soil containing 0.5 to 36 ppm each of TRCE and CBZ were heated to 88°-160°C (Section 4)

- 6-ft tall columns of jet fuel contaminated sandy soil were treated at 150°-160°C (Section 4)

- 200-1200 gm of spiked sandy soil containing PCB 1242 were treated at 150°-160°C (Section 5)

The chemical treatment of soil containing Aroclor 1260 by potassium polyethylene glycolate was investigated (Section 6) on 25 gm and 300 gm batches of spiked soil.

A detailed field-test design was prepared for heating 500 cu ft of sandy soil containing solvents and jet fuel. Cost studies were performed to allow comparison of the in situ RF heating process with excavation and incineration of the soil in a facility licensed to dispose of hazardous waste. It was shown that the RF process would be less expensive by a factor of 2 to 4.

In addition to the favorable economics and the benefits of in situ treatment processes mentioned earlier, the RF process has another significant advantage: extremely small amounts of gases and vapors which require treatment are produced. This is so, because the vaporized contaminants are not diluted by heat transfer fluids or products of fuel combustion. Thus, a small-volume high-concentration liquid waste stream is produced during treatment of the gases and vapors.

The purpose of this final report is to present the results of the bench- and pilot-scale experiments and economic studies through which the feasibility of in situ treatment of soil using the RF heating process was established.

SECTION 2

DECONTAMINATION OF SOILS CONTAINING SOLVENTS AND FUELS

INTRODUCTION

Soils contaminated with various chlorinated hydrocarbons, aromatic hydrocarbons, and jet fuels are found at several Air Force bases. Similar types of contaminants including gasoline are found in soils at sites of old storage tanks, petrochemical plants and refineries. Typical examples of hazardous contaminants found in soil are: tetrachloroethylene (TRCE), dichloroethane, trichloroethylene, benzene, chlorobenzene, and components of JP-4 jet fuel. These materials boil in a temperature range of 80° to 232°C, and can be readily volatilized by increasing their temperature. The purpose of the experiments described in Sections 3 and 4 was to establish the technical feasibility of removing these contaminants from the soil and recovering them under the action of heat. Recovery of the contaminants will occur from vaporization, distillation, and steam distillation caused by native moisture in the soil. The heating of the soil can be accomplished by using in situ radio frequency (RF) heating techniques.

In this section, a discussion of a theoretical basis for the removal of the above-mentioned contaminants under the action of heat is given. The emphasis is on why contaminants with high boiling points can be recovered as vapors at temperatures which are significantly below the normal boiling point of the materials. A brief description of the types of feasibility experiments performed on sandy soil containing fuels and solvents is also given in this section.

THEORETICAL BASIS FOR THERMAL RECOVERY OF CONTAMINANTS

A volatile organic solvent may be removed and recovered from soil under the action of heat by the combined effect of up to three mechanisms:

- Volatilization
- Steam distillation
- Steam stripping.

Volatilization

This refers to the loss of mass from a liquid phase of a substance to the vapor phase due to its vapor pressure. In a closed system where the vapors are confined in contact with the liquid, volatilization of the liquid soon reaches an equilibrium. In this state, there is no net transfer of the substance from the liquid to the vapor because an equal and opposite transfer occurs from the vapor to the liquid phase. However, in an open system where the vapors are free to escape, equilibrium is never achieved and a net rate of liquid vaporization is observed. In such a situation, the partial pressure of the vapors in the gaseous state is nevertheless related to the saturation vapor pressure of the component which is determined by the temperature. At low temperatures, the rate of volatilization can be expected to be small because of the low vapor pressure and hence low partial pressure. The volatilization rate can be increased, however, by increasing the temperature to raise the vapor pressure. Another method of increasing the rate is by continuously removing the newly formed vapors by a variety of means such as: a fan, a blower, or by a flowing gas sweep, etc. When liquid is mixed with soil, the rate of volatilization will not be the same as that of a pure liquid at the same temperature. This is due to reduction in the vapor pressure of the liquid caused by adsorption and capillary effects. Nevertheless, raising the temperature and/or providing a flowing gas sweep will increase the rate of vapor formation.

Steam Distillation

This refers to the reduction in the boiling point of a mixture of water and another component which is present in sufficient concentration such that two liquid phases are present. For example, when benzene is mixed with water, the mixture boiling point is less than the normal boiling point of either water or benzene. The reduction in boiling point occurs because each component exerts its own vapor pressure, independent of the presence of the other component. The two-phase mixture begins to boil when the sum of the partial pressures of all components equals 760 mm Hg. The reduction in boiling point and the quantity of steam necessary for distillation can be calculated from thermodynamic considerations. Table 1 shows the results of such calculations for binary mixtures of various simple hydrocarbons with water. As shown by the table, reasonable quantities of steam are required for pure components that boil up to 150°C.

For hydrocarbons with vapor pressures of one or two orders of magnitude less than that of water, the steam requirement increases to more than a pound of steam per pound of the hydrocarbon. But, the results show that the quantity of steam required for steam distillation can be provided by native water naturally occurring in soils. This is because of the low concentration of contaminants that occur in soil. For example, consider 100 grams of soil containing 5 percent water and 100 ppm TRCE. The steam to TRCE ratio required for steam distillation is 0.19 versus a water-to-tetrachloroethylene ratio of 500 in the soil.

TABLE 1. BOILING POINT REDUCTION AND THEORETICAL STEAM CONSUMPTION DURING STEAM DISTILLATION

Component	Mixture Boiling Temperature, °C	Pure Component Boiling Point, °C	lb Steam/ lb Component
Benzene	68.3	80.1	0.092
Toluene	83.9	110.6	0.236
TRCE	87.7	120.8	0.19
Bromoform	94.3	150.0	0.311
Hexachloroethane	98.7	186.0	1.57

Steam Stripping

Steam stripping can effectively remove contaminants from soil by providing a mechanism for improving the rate of volatilization of the contaminant in the presence of steam. The vapor pressure of most hydrocarbons at 100°C is quite high and appreciable volatilization rates can be achieved if the contaminant vapors are prevented from equilibrating with the liquid.

Generation of steam by boiling native moisture can help by providing a gas sweep that continuously removes the contaminant vapors. Steam-stripping can be used to improve the vaporization rate of those contaminants that cannot be steam-distilled, either because they are miscible with water or because their concentration is less than the solubility limit, so that a two-phase system is not formed.

TYPE OF FEASIBILITY EXPERIMENTS

Feasibility of soil decontamination by thermal treatment was determined through bench- and pilot-scale experiments. Four different types of experiments were performed with increasing levels of complexity. Table 2 summarizes the four different types of experiments. In the bench-scale, clean soil was contaminated with TRCE or TRCE and chlorobenzene (CBZ) spikes. These experiments are described in Section 3. For pilot-scale experiments, spiked as well as jet fuel contaminated soils were used. Pilot-scale experiments are described in Section 4. All experiments were performed on sandy soil, which was selected because it represented the soil type at contaminated sites at which the first field test of the process would be conducted.

TABLE 2. TYPE OF FEASIBILITY EXPERIMENTS PERFORMED

Experiment Scale	Soil		Contaminants	Concentration Level
	Type	Source		
Bench	Sandy	Tyndall AFB, FL	TRCE	10 and 1000 ppm
Bench	Sandy	Volk ANGB, WI	TRCE/CBZ	10 ppm
Pilot Scale	Sandy	Volk ANGB, WI	TRCE/CBZ	0.5 to 40 ppm
Pilot Scale	Sandy	Volk ANGB, WI	Jet Fuel	Up to 4000 ppm

TRCE = tetrachloroethylene

CBZ = chlorobenzene

SECTION 3

BENCH-SCALE EXPERIMENTS ON SOLVENTS AND FUELS

The purpose of performing these experiments was to determine whether TRCE and CBZ could be removed from soil by a combination of steam distillation or steam stripping using native moisture levels present in the soil.

As mentioned in Table 2 (page 7), experiments were performed with 25 gm of sandy soil containing TRCE, or TRCE and CBZ in the concentration range of 10 to 1000 ppm. Soil decontamination was investigated in a treatment temperature range of 88° to 135°C, and an initial soil moisture range of 5 to 10%. The above temperature range represents the steam distillation temperature for TRCE (88°C) and the normal boiling point of CBZ (132°C).

The results of the experiments show that 94 to 99% removal of the contaminants is feasible in the above temperature range in a soaking time of 3.5 to 4.0 hours. Mass balance closure in the range of 70 to 104% was obtained for each contaminant in these experiments.

The bench-scale experiments have established the technical feasibility of decontaminating soils containing chlorinated solvents by relatively low temperature thermal treatment.

A four-step experimental procedure was used:

- Spiking of soil to obtain the desired initial concentration
- Thermal decontamination experiments
- Recovery and analysis of vapors (distillate) generated during the experiment to determine the amount of contaminant vaporized.
- Analysis of treated soil to determine residual concentration in soil.

The experimental procedure and the results of the bench-scale experiments are discussed below.

SPIKING OF SOIL

In all the experiments 75 grams of moist soil was spiked with a solution of TRCE or TRCE and CBZ in pesticide grade hexane. The soil moisture content was typically 5.7% by weight. The soil was placed in a round-bottomed flask and weighed. A measured volume of the spiking solution was added to the flask. The quantity of the spiking solution added was based on the analysis of the solution, the quantity of soil in the flask, and the desired concentration level. After addition of the spike, the flask was sealed and tumbled in an ice bath for three hours to homogenize the soil and the spike.

PROCEDURE FOR DECONTAMINATION EXPERIMENTS

The experimental setup for the decontamination experiments is shown in Figure 1. The flask containing the tumbled, spiked soil was attached to a condenser, as shown in the figure. A thermocouple was firmly taped to the bottom of the flask and used for controlling the outer wall temperature. Another thermocouple was placed in the thermowell to measure the soil temperature. A small quantity (~ 1.0 ml) of mineral oil was placed in the thermowell.

The distillate removal tube of the condenser was attached to a volumetric flask (distillate receiver) in which ~ 10 ml of pesticide grade hexane was placed. The distillate recovery tube was allowed to extend into the volumetric flask as shown. The distillate receiver was placed in an ice bath. A Tenax® trap was attached to the condenser gas outlet to trap any uncondensed contaminant vapors.

The experiment was begun by heating the flask with an electric heating mantle. The power to the heater was regulated by a variac. The outer-wall thermocouple and a proportional controller were used to control the outside temperature. The soil was heated to the final temperature (as measured by the thermocouple in the thermowell) and maintained for 3.5 to 4 hours.

At the end of the experiment, the soil was allowed to cool down to room temperature before the distillate receiver and the Tenax® trap were removed.

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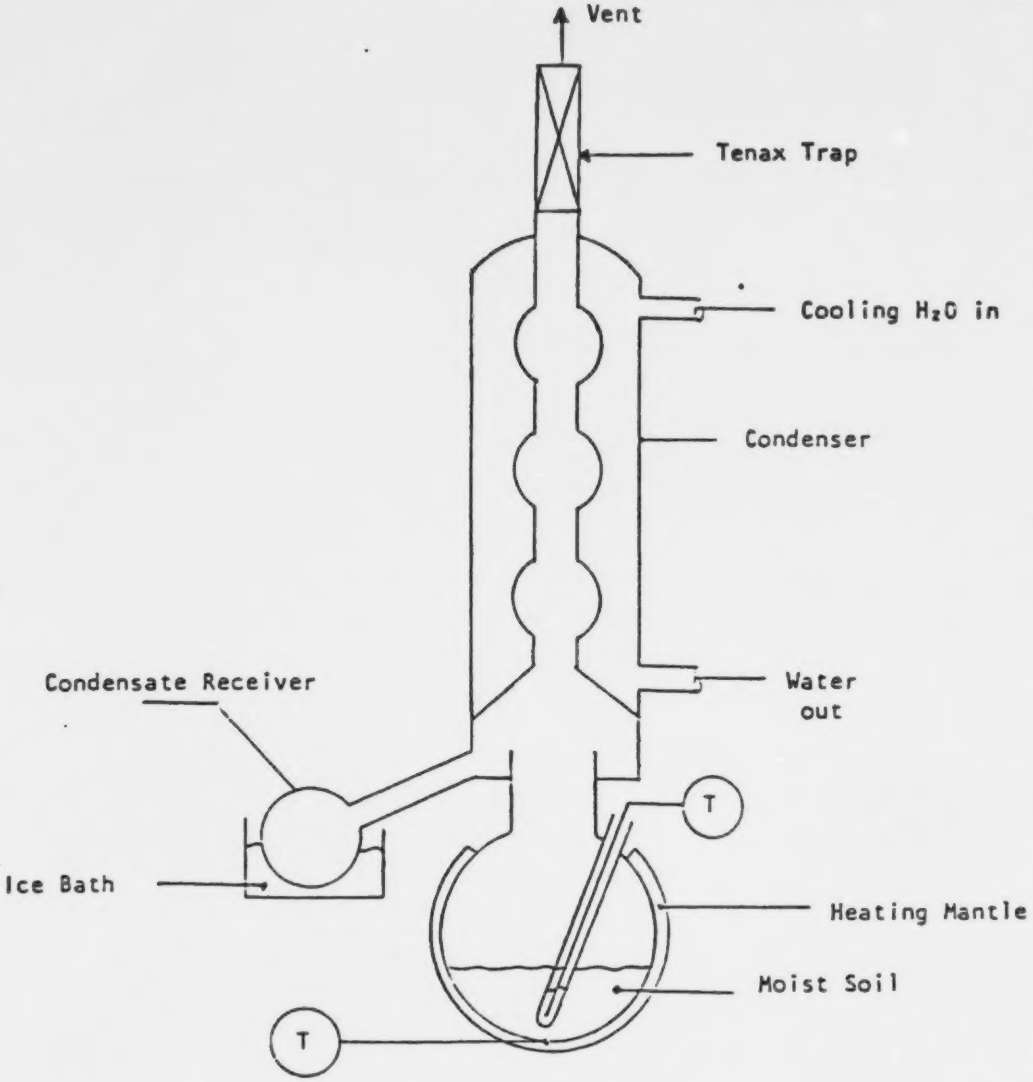
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Figure 1. Bench-scale soil decontamination set-up for solvents.

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RECOVERY AND ANALYSIS OF DISTILLATE

After disconnecting the receiver and the condenser from the flask containing the soil, all glassware and tubing that were wetted by contaminant vapors were rinsed with hexane. The interior surfaces of the condenser were rinsed with hydrocarbon-free water and hexane. The rinsate was combined with the distillate. The Tenax® trap was washed with approximately 20 ml of pesticide grade hexane. The washings were combined with the distillate. The distillate receiver now had two phases - the water phase and the hexane phase containing the contaminants.

To reduce sampling errors and ensure closure of mass-balance, the entire volume of distillate and rinsate was prepared for GC analysis. The alternative method of preparing a small portion of the distillate was not used because of concerns mentioned above. The first step in sample preparation was drying of the distillate to remove water which, if present, interferes with the operation of the GC or GC/MS. The water was removed by passing the entire quantity of the distillate and rinsate through a bed of anhydrous sodium sulfate. Although the drainage rate of the distillate through the bed was extremely slow, it was found that if the water phase was frozen out of the distillate the drainage rate would improve. The following procedure was used to allow drying of the entire volume of distillate and rinsate in a reasonable amount of time. After recovery the distillate receiver was stoppered and placed in a freezer and the aqueous phase was allowed to freeze. The hexane phase was then decanted and dried by passing it through a bed of anhydrous sodium sulfate. Fresh hexane was added to the flask containing the frozen water phase. Once the ice melted, the entire contents of the flask were dried through the sodium sulfate bed. To ensure good recovery of the contaminants and minimize volatilization losses, all the containers and receivers used for handling the hexane phase were kept chilled in an ice bath. Similarly, after drying the hexane phase, the sodium sulfate bed was rinsed with fresh, chilled hexane to recover any contaminants retained in the pore space of the dryer bed.

The dried distillate was brought up to volume with hexane in a 100-ml volumetric flask. The distillate was analyzed for the contaminants using procedures described in Appendix A.

DETERMINATION OF RESIDUAL CONCENTRATION

Residual contaminant concentration in the soil was determined by the steam distillation-extraction procedure described in Appendix A. This was done by attaching the flask containing the treated soil to a Nielson-Kryger[3] distillation head. To avoid volatilization losses and sampling errors, the entire quantity of the treated soil was analyzed without transferring the soil from one flask to another.

RESULTS OF BENCH-SCALE EXPERIMENTS

As mentioned earlier, bench-scale experiments of two different types were conducted. In the first type, TRCE was the only contaminant present, whereas in the second type, both TRCE and CBZ were present.

Decontamination experiments were performed on soil at two TRCE concentration levels. For each experiment, the percent removal of the contaminant and percent mass balance closure were calculated using the following equations:

$$\text{Percent Removal of Contaminant} = \frac{(\text{Mass Initially Present} - \text{Mass Remaining in Soil})}{\text{Mass Initially Present}} \times 100$$

$$\text{Percent Mass Balance Closure} = \frac{(\text{Mass Recovered in Distillate} + \text{Mass Remaining in Soil})}{\text{Mass Initially Present}} \times 100$$

Results of both single (TRCE) and two (TRCE and CBZ) contaminant experiments show that 94 to 99% removal of the contaminants is feasible in the temperature range of 88° to 135°C in a soaking period of 3.5 to 4 hours. It was found that in the temperature range investigated, the removal of either contaminant was independent of temperature. This is a significant advantage because the results indicate that during in-situ decontamination the temperature of the soil need not be raised to the normal boiling point of the contaminants. Instead, temperatures which are lower than the normal boiling point may be utilized. The lower limit is probably defined by the lowest steam distillation temperature of the components present.

In each experiment, only 75 gms of soil was treated. Pilot-scale experiments (Section 4) have shown, however, that similar removal is obtained when tall columns of contaminated soil are subjected to similar treatment.

Single Contaminant Experiments

At the 957 ppm contaminant level, the effect of soil moisture content, and temperature on the degree of decontamination was studied. Results of all nine experiments (Table 3) show that significant removal of TRCE is feasible, although there were no significant effects from moisture content or temperature in the ranges studied. The effects of moisture content were studied at 5.7 percent and 9.9 percent; the effects of temperature were studied at three levels: 90°, 100°, and 130°C. The average removal of TRCE from soil in all nine experiments was 96.6 percent with a standard deviation of ± 2.0. The average final concentration in the soil after treatment was 38 ppm with a standard deviation of ± 17 ppm.

The last column in Table 3 gives the percent closure of the mass balance in each of the 11 experiments. The mass balance was established by analyzing the concentration of residual TRCE in the treated soil and by an analysis of the distillate. The total quantity of TRCE was calculated from these two results and compared with the total weight of TRCE in the original spike. There were two experiments in which the mass balance closures were 56 and 59 percent. It is suspected that these were caused by sample losses during handling. Unlike the third experiment in which the closure was only 61 percent, no obvious reasons could be determined for the 56 and 59 percent closure. The reason for 61 percent closure was a leak in the distillate recovery line.

The data in the last row of Table 3 are for a control experiment in which the soil was not heated. The results show that when the soil is not heated, there is no recovery of TRCE from the soil.

TABLE 3. RESULTS ON RECOVERY OF TETRACHLOROETHYLENE (TRCE) ON HEATING OF SOIL[a]

(Initial Concentration 957 ppm)

Run No.	Initial Soil Temp., °C	Wt % Moisture	Final Soil Temp. °C	Soaking Time, h	Final[b] Conc. in Soil, ppm	Wt of TRCE in Distillate, mg	Wt of TRCE Remaining in Soil, mg	% TRCE Removed From Soil	% Mass Balance Closure
93LT-1	24	5.7	101	2.9	40.6	71.9	2.87	96.0	104.1
95LT-2	19	5.7	101	3.6	18.4	73.3	1.30	98.2	103.9
913LT-3	24	5.7	101	3.6	29.1	42.0	2.05	97.1	[c]61.4
917LT-5	22	5.7	131	3.8	20.6	62.5	1.46	98.0	89.1
918LT-6	24	5.7	90	4.0	58.4	38.2	4.13	94.2	59.0
920LT-7	21	5.7	101	4.0	56.3	61.5	3.98	94.5	91.2
920LT-8	23	5.7	90	4.1	52.0	65.4	3.68	94.9	96.2
924LT-9	23	9.9	102	3.5	25.0	47.9	1.69	97.6	69.1
924LT-10	23	9.9	89	4.0	1.6	40.4	0.11	99.8	56.4
115LT-11[d]	23	5.9	21	4.0	1089	.026	76.5	0.4	103

[a] All runs with 75 gms of moist soil containing 957.3 ppm TRCE. Weight of TRCE in soil is 71.8 mg. Initial concentration reported on wet basis.

[b] Concentration reported on dry basis.

[c] Found a leak in the distillate recovery line.

[d] This experiment had 992 ppm TRCE in soil. Weight of TRCE in soil was 74.4 mg. Initial concentration reported on a wet basis.

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The amount of TRCE recovered in this control experiment is much lower than what would be expected based on the vapor pressure of pure TRCE at 22°C. This is probably due to the reduction of vapor pressure caused by adsorption of TRCE on soil.

The experiment plan at 1000 ppm was discontinued after nine runs because of the substantial recovery observed when these experiments were performed under conditions that had been expected to give less favorable results. Instead, additional experiments were performed on soils containing 9.28 ppm TRCE. The results of these additional experiments are presented in Table 4.

A total of five decontamination experiments (Table 4) were performed on soil containing 9.28 ppm TRCE. These experiments were performed at two temperature levels: 90° and 100°C. However, only one soil moisture level was investigated. The low value of 5.7 percent moisture was selected to compare data with the high contaminant concentration experiments. The low moisture level was also selected to represent the least favorable conditions for the steam distillation of TRCE from soil. Like the high concentration level experiments, substantial recovery of TRCE was observed in all the cases. The average recovery in these five experiments was 95 percent with a standard deviation of ± 1.5. The average residual concentration of TRCE in the soil was 483 ppb with a standard deviation of ± 147 ppb. Like the results of the high concentration experiments, the treatment temperature in the 90° to 100°C range was found to have equally high recovery efficiencies of TRCE.

The last line of data in Table 4 is for a control experiment in which soil containing 9.92 ppm TRCE was placed in the experimental apparatus but maintained at an average temperature of 22°C for a period of 4 hours. The results of this experiment show that there is no vaporization of TRCE when the soil is not heated.

Two Contaminant Experiments

TRCE and CBZ were spiked on clean (previously contaminated) sandy soil obtained from Volk Air National Guard Base, Camp Douglas, Wisconsin. All experiments were performed at initial concentration level of 9 to 10 ppm, soil moisture content of 5 to 6% and soaking time of 4 hrs. Soaking time refers to

TABLE 4. RESULTS ON RECOVERY OF TETRACHLOROETHYLENE (TRCE) ON HEATING OF SOIL[a]

(Initial Concentration 9.3 ppm)

Run No.	Initial Soil Temp., °C	Wt % Moisture	Final Soil Temp. (Avg) °C	Soaking Time, h	Final Conc. in Soil,[b] ppb	Wt of TRCE in Distillate, μg	Wt of TRCE Remaining in Soil, μg	% TRCE Removed From Soil	% Mass Balance Closure
103LTL-1	26	5.7	100	3.7	635	517	44.9	93.5	80.8
103LTL-2	22	5.7	101	3.5	525	596	37.1	94.7	91.0
107LTL-3	22	5.7	99	3.6	461	601	32.6	95.3	91.1
107LTL-4	19	5.7	90	3.7	499	498	35.3	94.9	76.6
109LTL-5	25	5.7	89	4.1	242	592	17.1	97.5	87.5
115LTL-9[c]	23	5.9	21	4.0	9690	2.3	684	0.3	92.2

[a] All runs with 75 gms of moist soil containing 9.28 ppm TRCE. Weight of TRCE in soil is 695.8 μg. Initial concentration reported on wet basis.

[b] Concentration reported on dry basis.

[c] Initial concentration of TRCE in soil 9.92 ppm, reported on a wet basis. Weight of TRCE in soil 744 μg.

the duration for which soil was maintained at the final temperature, excluding the heat-up time.

The results (Tables 5 and 6) of these experiments show that significant removal of both TRCE and CBZ is feasible when treated for 4 hrs in a temperature range of 90° to 135°C. This range was selected to represent the steam distillation temperature of TRCE and the normal boiling point of CBZ. The initial concentration of TRCE in these experiments was 9530 ppb while the residual concentration was in the range of 120-320 ppb. The initial concentration of CBZ was 9330 ppb while the residual concentration was 190-315 ppb, as shown in Table 5.

The data shown in the last line of Table 5 are for a control experiment in which soil was kept in the flask for 4 hrs at 25.3°C. As the results show, no removal of either contaminant occurred.

Mass balance and percent removal were calculated for all experiments. This is summarized in Table 6. In all experiments (except the control), 96.8 to 98.8% removal of TRCE and CBZ was observed. For both components, good mass balance closure was obtained in all but one experiment. In the second experiment at 90°C, neither TRCE nor CBZ were detected in the distillate obtained from the experiments, whereas analysis of residual concentration in soil shows that 97-98% removal had occurred. It would appear that there was a leak in the joints between the condenser and the condensate receiver shown in Figure 1.

CONCLUSIONS AND RECOMMENDATIONS

The bench-scale experiments performed with one and two contaminants present in sandy soil have established the feasibility of cleaning such soils by relatively low-temperature thermal treatment. It was shown that 95-98% of TRCE and CBZ can be removed from soil in reasonable time periods, even when the temperature is 30° to 40°C less than the normal boiling points of these contaminants. Although these results are encouraging for the treatment of sandy soils, similar studies are required for different types of soil such as clayey and loamy soils.

TABLE 5. RESIDUAL SOIL CONCENTRATION FOR TRCE AND CBZ (75-GRAM SCALE)

Moisture, wt%	Initial Concentration,* ppb		Final Soil (Avg.) Temp., °C	Soaking Time, hr	Final Conc.** in Soil, ppb		Remarks, Exp. #
	TRCE	CBZ			TRCE	CBZ	
5.42	9530	9330	89	4	121	191	VS8-1-86-1
5.42	9530	9330	88.2	4	155	246	VS8-1-86-2
5.42	9530	9330	134.2	4	320	315	VS8-8-86-1
5.42	9530	9330	129.1	4	287	273	VS8-8-86-2
5.42	8780	8580	25.3	4	9360	8710	VS8-19-86-1

*Based on analysis of spike solution.

**On dry basis.

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TABLE 6. MASS BALANCE AND REMOVAL OF TRCE AND CBZ

Experiment No.	Weight Initially Present in Soil, µg		Wt Recovered in Distillate, µg		Wt Remaining in Soil, µg		Removed From Soil, %		Mass Balance, %		Remarks
	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ	
VS8-1-86-1	715	699.6	657.9	633.6	8.61	13.54	98.8	98.1	93.2	92.5	At 90°C
VS8-1-86-2	715	699.6	n.d.	n.d.	11.02	17.44	98.5	97.5	1.5	2.5	At 90°C
VS8-8-86-1	715	699.6	659.9	625.5	22.68	22.31	96.8	96.8	95.5	92.6	At 130°C
VS8-8-86-2	715	699.6	664.8	637.5	20.39	19.37	97.1	93.9	95.8	93.9	At 130°C
VS8-19-86-1	658.6	643.6	3.0	3.25	702	653.9	-	-	107	102	At room temperature

n.d. = Not detected.

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Studies are also needed to determine whether other types of contaminants, especially those with attached polar groups, can be as easily removed from the soil.

Successful closure of mass balance on TRCE and CBZ indicates that no significant chemical reactions involving these species occurred under the time-temperature treatment conditions that were studied.

The bench-scale experiments were performed on thin soil beds. For the process to work under in-situ conditions, feasibility experiments are necessary on tall columns of soil. The purpose is to verify that the vaporized contaminants will move up through the soil bed for collection at the surface. The other purpose is to demonstrate uniformity of decontamination along the length of the bed. If this is feasible, then a simple design for the recovery and containment of the contaminant vapors from the soil surface can be devised. Pilot-scale experiments to address these issues are described in Section 4.

SECTION 4

PILOT-SCALE EXPERIMENTS ON SOLVENTS AND FUELS

In the bench-scale experiments, the soil bed was no more than 2 to 3 in. thick. This made it relatively easy for the contaminant vapors to move up through the soil bed for recovery in the condenser. However, in the field, the vapors would have to move up to the surface through the thickness of the heated zone for collection at the surface.

The purpose of performing the pilot-scale experiments was, therefore, to demonstrate that at least 95% of the contaminants can be removed from tall soil beds by contaminant vaporization and recovery at the top surface. A 6-ft soil bed was used. This height was selected based on the preliminary designs of a field test at the Volk Air National Guard Base (ANGB), Camp Douglas, Wisconsin, in which it was planned to heat soil to a depth of 6 to 8 ft.

Pilot-scale experiments were performed on soil spiked with contaminants as well as soil obtained from Volk ANGB. The field soil was contaminated with jet fuel. The spiked soil was prepared by adding solutions of CBZ and TRCE to clean (previously uncontaminated) sandy soil which was also obtained from Volk ANGB.

Results of the pilot-scale experiments using spiked contaminants have shown that it is feasible to remove greater than 99% of the contaminants from the soil. These experiments were performed on soil containing 0.5 to 36 ppm of TRCE and CBZ, in a temperature range of 130° to 160°C. It was also shown that the contaminants can be recovered at the top surface of the soil bed and a residual concentration profile does not develop along the length of the heated 6-ft tall soil column.

Soil containing jet fuel (JP-4) was decontaminated similarly by treatment in a temperature range of 152°-157°C for a period of 14 to 40 hours. Jet fuel has a normal boiling point of 80°-230°C, but 90 to 99% decontamination was demonstrated in the treatment temperature range mentioned above. It was shown that high boilers such as pentadecane can be recovered more efficiently by providing a steam sweep created by water injection at the base of the heated bed. Without water injection, 75% removal of pentadecane was observed, but with water injection 94% removal was achieved.

The results of the pilot-scale experiments have demonstrated the feasibility of in-situ treatment of sandy soils containing fuels and solvents. A design was prepared for an in-situ decontamination field test at Volk ANGB, WI. In this design provision was made for injection of water into the heated soil to assist in the removal of heavy boilers, if required. This design is described in Section 11.

The soil preparation methods, experimental procedures and results are discussed in the following sub-sections.

SOIL PREPARATION

As mentioned above, experiments were performed by spiking clean soil as well as on contaminated soil containing jet fuel. The purpose of soil preparation was to adjust soil moisture content and to spike it with 10 ppm of each of TRCE and CBZ. No soil preparation was performed for experiments in which contaminated soil from the field was used.

Preparation of Spiked Soil

Four experiments were performed on spiked soil. In each experiment, 3.5 to 4 kg of soil was used. It was found that large quantities of soil could not be reliably spiked at 10 ppm level because of high volatility of the contaminants, which leads to very high contaminant loss. Evidence of this was provided through measurement of initial soil concentration and inability to close mass balance. It is suspected that contaminant loss occurred due to vaporization at each of several material handling steps necessary to make the spiked soil. Two different methods were used to prepare the soil. In the first method, four 1-kg batches of soil were separately spiked, then mixed together. In the second method, one 5-kg batch was prepared for each experiment. In either case, the observed initial concentration of the spikes in soil ranged from none detected to 106.6% of the desired initial concentration level.

Soil Preparation by Method I--

Four separate 1-kg batches of soil were made for each experiment. The moisture content of the batch was adjusted first, by measuring the initial moisture content of soil, by adding the required amount of hydrocarbon-free water to give approximately 5% moisture and by confirming the moisture content by re-analyzing samples obtained from each batch.

The contaminants were spiked after soil moisture content was adjusted. The soil was spiked with a known volume of a gravimetrically prepared solution of CBZ and TRCE in hexane. The volume of spiking solution used was adjusted to give an initial concentration of 10 ppm of each of the two contaminants.

Each time the soil was spiked with water or the contaminants, it was tumbled to homogenize the soil. A sealed glass or Teflon® jar containing approximately 1 kg of soil was placed horizontally on a ball-mill roller. Each batch was tumbled for a period of 2 hours. This method required the separate preparation of four batches of soil for each experiment. When this method was used, all the 4 batches were combined in a Teflon® bag and further mixed by tossing the soil inside the bag. The mixed soil was then loaded into the reactor. Two samples of soil were removed from the bag to determine the initial concentration of the contaminants. This method of soil preparation was used for Experiment 1 in which glass tumbling jars were used and also for Experiment 2 in which Teflon® jars were used.

Several problems were encountered during the preparation of soil with the above method. These are:

- The soil tends to form a cake on the walls of the glass jar and does not tumble properly even when the jar is hit with a mallet. This requires longer tumbling time to homogenize. This problem was solved by using the Teflon® jar.

- It was found that there was considerable loss of the contaminant spike during the various preparation steps. Thus, the actual initial concentration of the contaminants in the soil was only 5% of the expected concentration based on the concentration of the spiking solution. This problem persisted even in the Teflon® jar.

Soil Preparation by Method II--

To resolve the second problem, the soil mixing procedure was changed so that only one 5-kg batch of soil was prepared per experiment instead of four 1-kg batches per experiment. It was expected that by reducing the number of steps requiring transferring soil from one container to another, volatilization losses would be minimized. The 5-kg batches were prepared in a stainless steel V-blender. To decrease contaminant volatilization losses even further, the spiking solution solvent was changed from hexane to the higher boiling decane. And finally, the initial spiking levels were increased from 10 ppm to 50 ppm for each of the two contaminants. The modified method was used for Experiments 3 and 4.

The method of sampling the soil was also changed for Experiments 3 and 4. For Experiments 1 and 2, the samples were obtain from the Teflon® bag prior to loading the reactor. For Experiments 3 and 4, the samples were obtained from the funnel used for pouring the soil into the reactor. Four grab samples were taken at different times from the funnel as the soil was being packed. The four samples were combined in a sealed jar, tumbled and then split into two aliquots of 75 gm each. These two aliquots were analyzed to determine the initial soil concentration.

It was found that even with the new equipment and procedures, extensive loss of the spiked contaminants occurred as determined by an analysis of the soil samples.

Preparation of Field Samples

Soil containing jet fuel was obtained from the Fire Training Pit located at Volk ANGB. Soil was obtained by drilling holes through the contaminated zone with a bucket-auger. The samples were stored in 0.25-gal glass jars with a Teflon®-lined screw cap. All samples were kept in an ice box until use. Each jar had approximately 1.0-1.5 kg of soil.

The experiments were performed by packing 3.5-4.0 kg of contaminated soil. As a result, more than one jar was needed to pack the reactor. Prior to packing the reactor, samples of soil were taken from each jar. Soil samples were obtained by inserting a glass tube all the way into the soil. The soil contained in the tube was transferred to a sealed Teflon® jar. All samples obtained from all jars used in each experiment were combined in the Teflon® jar and tumbled on a ball-mill roller. From the tumbled sample, two 150-gm aliquots were obtained for determination of initial soil concentration by the Nielson-Kryger steam distillation method.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The pilot-scale experiments were performed by packing 3.5-4.0 kg of contaminated soil in a stainless steel pipe reactor of diameter 1.5 in. and length 6 ft. External heating tapes, thermocouples, and insulation were added. The top of the reactor was connected to a glass water-cooled condenser equipped with a condensate recovery leg as shown in Figure 2. The condensate was collected in a chilled receiver. A Tenax® bed was attached to the gas outlet port of the condenser to trap any uncondensed vapors.

Two temperature controllers were used to control the temperature of the reactor as well as that of the vapor line connecting to the condenser.

In all the experiments, water was injected at the base of the soil column. Prior to water injection, the receiver was replaced with a new empty receiver. In one experiment, the soil was maintained at two different temperatures prior to steam injection. In this case, the distillate receiver was changed each time the temperature was changed and also prior to steam injection.

At the end of the experiment, the reactor was allowed to cool down before disconnecting the condenser. During the cool down period, the vapor interconnect lines were kept heated. The condenser and the vapor lines were disconnected when the soil had returned to room temperature. The vapor lines, the interior of the condenser, the Tenax® trap, and the distillate line were thoroughly rinsed with hexane. These rinsates were combined with the distillate from the last receiver, which, in all the experiments, contained condensate recovered after water injection.

The cooled soil was removed from the reactor over a long mylar sheet. An attempt was made to obtain the concentration as a function of depth. This was done by moving the inclined open reactor over the mylar sheet. The

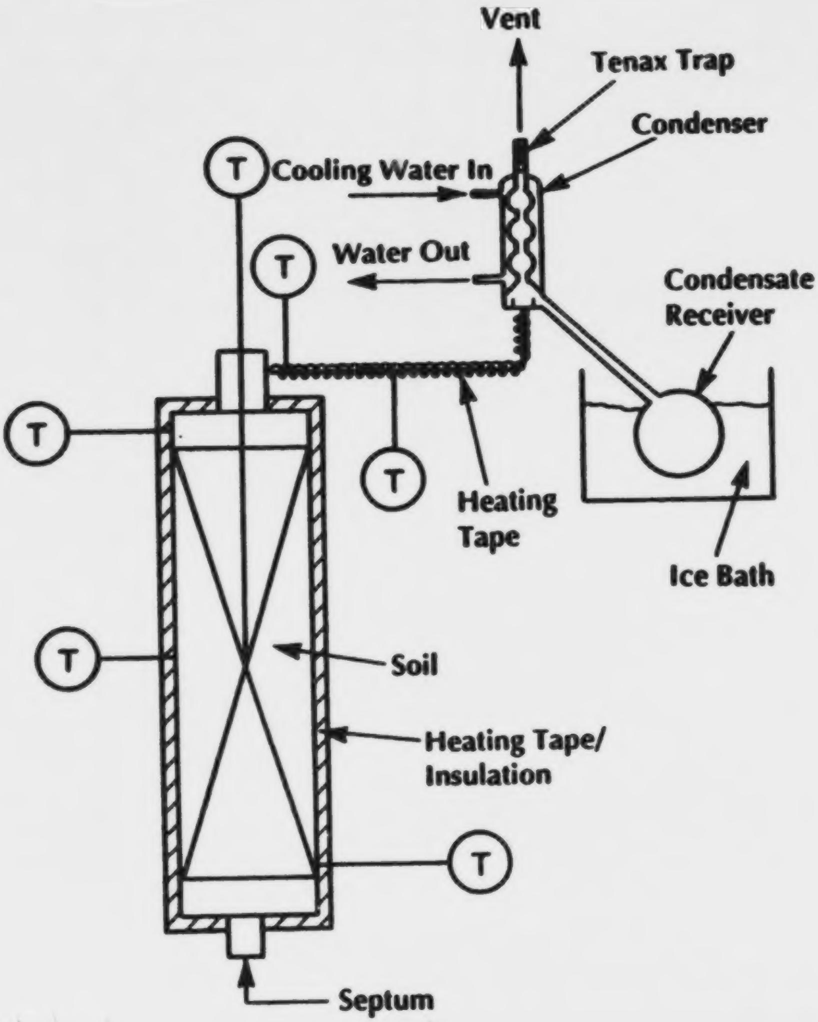
Vent
Tenax Trap
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Figure 2. Pilot-scale soil decontamination set-up for solvents and fuels.

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direction of reactor movement was opposite to the direction of soil motion. In this fashion, a bead of soil was laid out over the mylar sheet. The length of the bead was measured and then 75 gm samples were taken from the two extreme ends and the middle of the bead, representing the top, bottom, and middle of the soil when packed. In addition, the remaining soil was placed in a sealed glass jar, tumbled, and sampled to obtain an "average" sample for the entire bead. All the removal calculations are based on the analysis of the "average" soil sample.

EXPERIMENTAL CONDITIONS

The experimental conditions for four spiked-soil experiments are presented in Table 7. Two pilot-scale experiments were performed using contaminated soil containing jet fuel obtained from the field. The conditions of these two pilot-scale experiments are shown in Table 8. In five of the six pilot-scale experiments, water was injected at the base of the soil column and recovered as vapors at the top. The purpose of water injection was to determine whether any improvement in the degree of decontamination occurs due to steam sweep. Water injection was begun only after an initial soaking period of the heated soil column in a temperature range of 120°-160°C.

TABLE 8. EXPERIMENTAL CONDITIONS FOR REMOVAL OF JET FUEL

			Elapsed Time		
Exp. No.	Weight of Soil gm	Temp., °C	Before Water Injection, hrs	After Water Injection, hrs	Water Injection ml
5	3968.0	157	14.4	0.0	0.0
6	4022.0	152	17.4	0.0	0.0
6	4022.0	157	0.0	23.0	54

TABLE 7. PILOT-SCALE EXPERIMENTAL CONDITIONS FOR REMOVAL OF CBZ AND TRCE

Exp. #	Wt. of Soil, gm	Initial Concentration, ppm		Temp., °C	Elapsed Time Before Water Injection, hrs	Elapsed Time From Water Injection to Shut-down, hrs	Water Injected, ml
		TRCE	CBZ				
1	3923.0	0.1716	n.d.*	130	100.68	6.42	24
2	3654.0	0.5674	n.p.**	137	49.65	7.07	37.8
3	3458.4	34.45	36.4	159	18.07	21.51	18.4
4	3633.0	9.5	10.66	128	15.67	-	-
4				153	30.42	15.92	20

*n.d. = Not detected.

**n.p. = Not present.

PILOT-SCALE RESULTS

Results of pilot-scale experiments performed with soil spiked with CBZ and TRCE are given in the section below. Results of experiments performed with soil containing jet fuel are described on page 33.

Spiked-Soil Experiments with CBZ and TRCE

The results of Experiments 2, 3, and 4 are summarized in Table 9. Experiment 1 did not yield good results because the initial concentration of the TRCE was only 0.17 ppm and CBZ was below detection limit. This is probably related to the soil preparation problems described in a previous section. In Experiment 2, the initial TRCE concentration in soil was 0.57 ppm. Due to an oversight, CBZ was not spiked in this soil. The soil was heated to 137°C from room temperature at a rate of 4.4°C/hr. It was maintained at 137°C for a period of 50 hrs. At the end of this time period, approximately 2600 µg of TRCE were recovered as distillate. The distillate receiver was then replaced prior to water injection. Approximately 38 ml of water were injected. No additional TRCE was collected in the second distillate receiver. Analysis of soil taken from the reactor at end of the experiment showed that the concentration of TRCE had been reduced below the detectable limits.

In Experiments 3 and 4, the new method of soil preparation was utilized, using the stainless steel "V-blender." The target initial level of spiking was 50 ppm each of TRCE and CBZ. The actual initial concentrations in Experiment 3 were: TRCE 34.5 ppm and CBZ 36.4 ppm. In Experiment 3, the soil was heated to 151°C at a rate of 19°C/hr. The soil was maintained at 151°C overnight for a period of 18 hrs. At that time, it was observed that the temperature at the top and bottom of the reactor was approximately 30°C cooler than the middle. To increase the bottom and top temperatures, the temperature of the entire bed had to be raised such that the temperature inside the center of the bed was 167°C. Water injection was begun as soon as the center temperature reached 167°C. Approximately 18 ml of water were injected. The amount of TRCE recovered as distillate prior to steam injection was 92,725 µg,

TABLE 9. PILOT-SCALE EXPERIMENTAL RESULTS (SPIKED SOIL)

Exp. #	Wt. of Soil, grams	Initial Wt. in Soil, (μg)		Temp. of Soil Bed, °C	Wt. Recovered in Distillate Before Water Injection (μg)		Wt. Recovered in Distillate After Water Injection (μg)		Wt. Remaining in Soil (μg)		Removed From Soil, %		Mass Balance %	
		TRCE	CBZ		TRCE	CBZ	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ
1	3923.0	701.24	n.d.	130	15.43	n.d.	n.d.	n.d.	NA	NA				
2	3654.0	2106.2	n.p.	137	2607.5	n.p.	n.d.	n.p.	n.d.	n.p.	100		124	-
3	3458.4	124,106	131,131	159	92,725	86,675	272.3	139.3	n.d.	n.d.	100	100	75.05	66.45
4	3633.0	35,951.56	40,341.44	128	78,875	92,000								
				155	11	9.75	61	63.75	206.45	641.1	99.4	98.4	220.2	240.98

n.d. = Not detected.

n.p. = Not present.

NA = Not applicable.

and the amount of CBZ recovered was 86,675 μg. After steam injection, the amount of TRCE and CBZ recovered was 272 and 139 μg, respectively. The analysis of soil from the reactor after the experiment showed that the concentration of TRCE and CBZ had been reduced below the detectable limits. These results are summarized in Table 9.

In Experiment 4, the initial concentration of soil was 9.5 ppm TRCE and 10.7 ppm CBZ based on an analysis of two initial soil samples. The soil was initially heated to 123°-131°C at a rate of 17.1°C/hr. It was maintained in this range for a period of 15.7 hrs. At the end of this time, the distillate receiver was found to contain 78,875 μg of TRCE and 92,000 μg of CBZ. The temperature was raised to 153°C and maintained for a period of 30.4 hrs. At the end of this time, only 11 μg of TRCE and 9.75 μg of CBZ were collected. This shows that there is no need to heat the soil to 150°C for these contaminants.

Approximately 20 ml of hydrocarbon-free water were injected, and the soil was kept at 153°C for 16 hrs after steam injection. After steam injection, an additional 61 μg of TRCE and 64 μg of CBZ were collected in the distillate receiver. The soil analysis after the treatment was 0.06 ppm TRCE and 0.19 ppm CBZ.

Samples of soil were taken by emptying the reactor over a mylar sheet and forming a long bead of soil. The samples obtained from the two ends of the bead and from the middle were analyzed separately to estimate whether a vertical concentration profile had developed in the soil. Three such samples were obtained from all four experiments. The results of these samples are shown in Table 10. The conclusion is that a vertical residual concentration profile does not develop in the soil bed.

TABLE 10. RESIDUAL CONCENTRATION OF TRCE AND CBZ AS A FUNCTION OF SOIL DEPTH (SPIKED SOIL EXP.)

Exp. #	ppm Concentration in Spent Soil - Top		Concentration in Spent Soil - Middle		Concentration in Spent Soil - Bottom		Average Concentration in Spent Soil	
	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ	TRCE	CBZ
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	n.d
3	n.d.	(BDL) 0.03	0.04	0.1	0.04	0.09	n.d.	n.d.
4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	0.18

n.d. = Not detected.

bdl = Below detection limit.

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Jet Fuel-Contaminated Samples

Two experiments (Nos. 5 and 6) were performed in the pilot-scale with soil contaminated with jet fuel. This soil was obtained from the Fire Training Pit located at Volk ANGB.

In Experiment 5, the soil was heated to 157°C from room temperature at an average rate of 15.2°C/hr. It was maintained at 157°C for a period of 14.4 hrs. The time-temperature history for this experiment is shown in Figure 3. The experimental conditions were summarized in Table 8 (page 27).

In Experiment 6, the soil was heated to 152°C from room temperature at an average rate of 21.6°C/hr. The time-temperature history of this experiment is shown in Figure 4. The soil was maintained at 152°C for a period of 17.4 hrs. At the end of this time period, the distillate receiver was replaced to start the water injection. Approximately 54 ml of water were injected. The water injection was done over a period of 1.63 hrs. After the water injection, the reactor was maintained at 157°C for a period of 23 hrs.

At the end of each experiment, the reactor was allowed to cool down before disconnecting the condenser. During the cool-down period, the vapor interconnect lines were kept heated. The condenser and the vapor line were disconnected when the soil had returned to room temperature. The vapor lines, the interior of the condenser, the Tenax® trap, and the distillate line were thoroughly rinsed with hexane. In Experiment 5, the rinsates were combined with the distillate from the receiver. However, in Experiment 6, three distillate samples were prepared. These were: the distillate from the first receiver before water injection, the distillate from the second receiver after water injection, and finally, the rinsate of the vapor lines, the interior of the condenser, the Tenax® trap, and the distillate line.

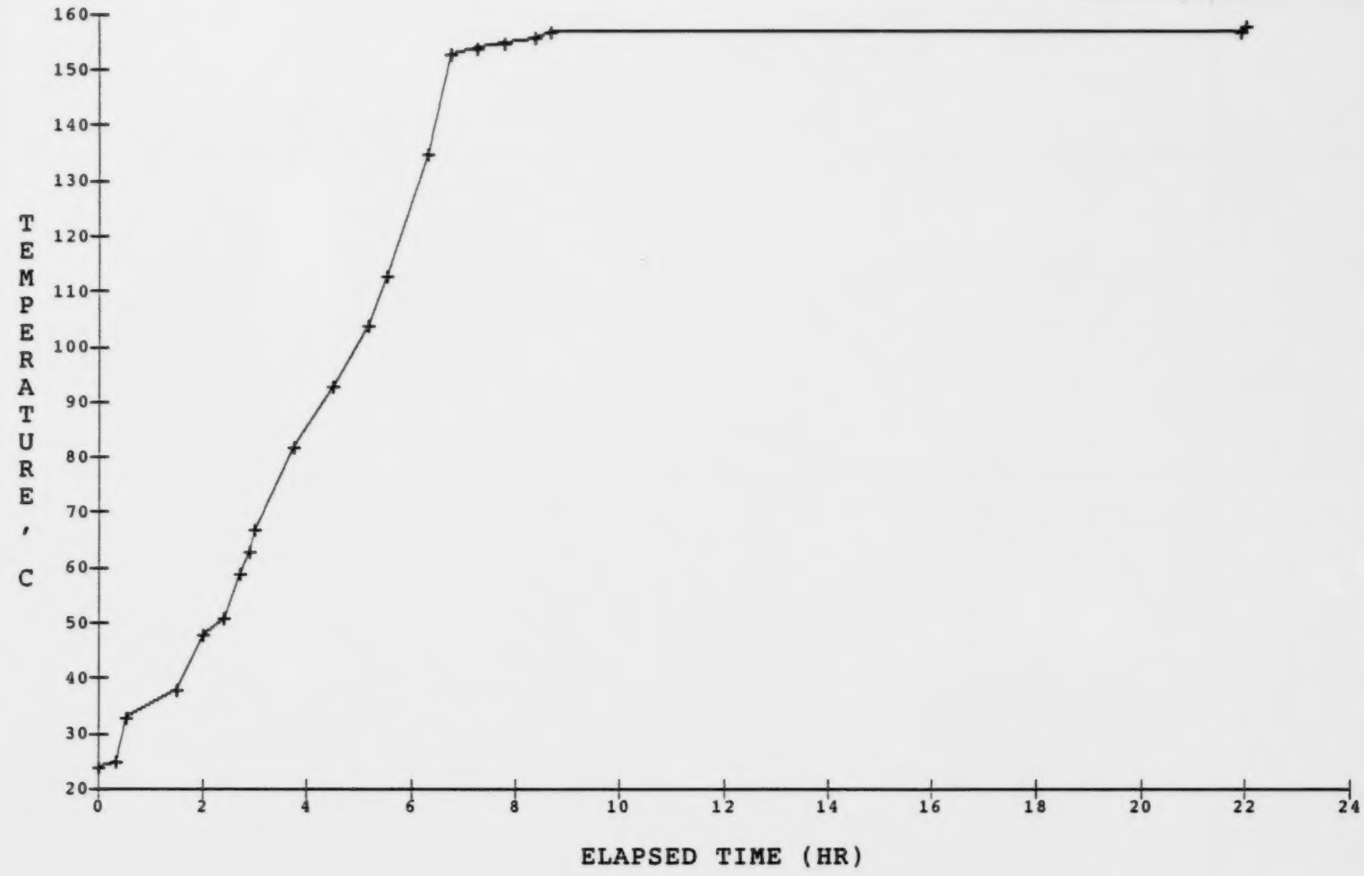

Figure 3. Temperature history for jet fuel decontamination (Experiment No. 5).

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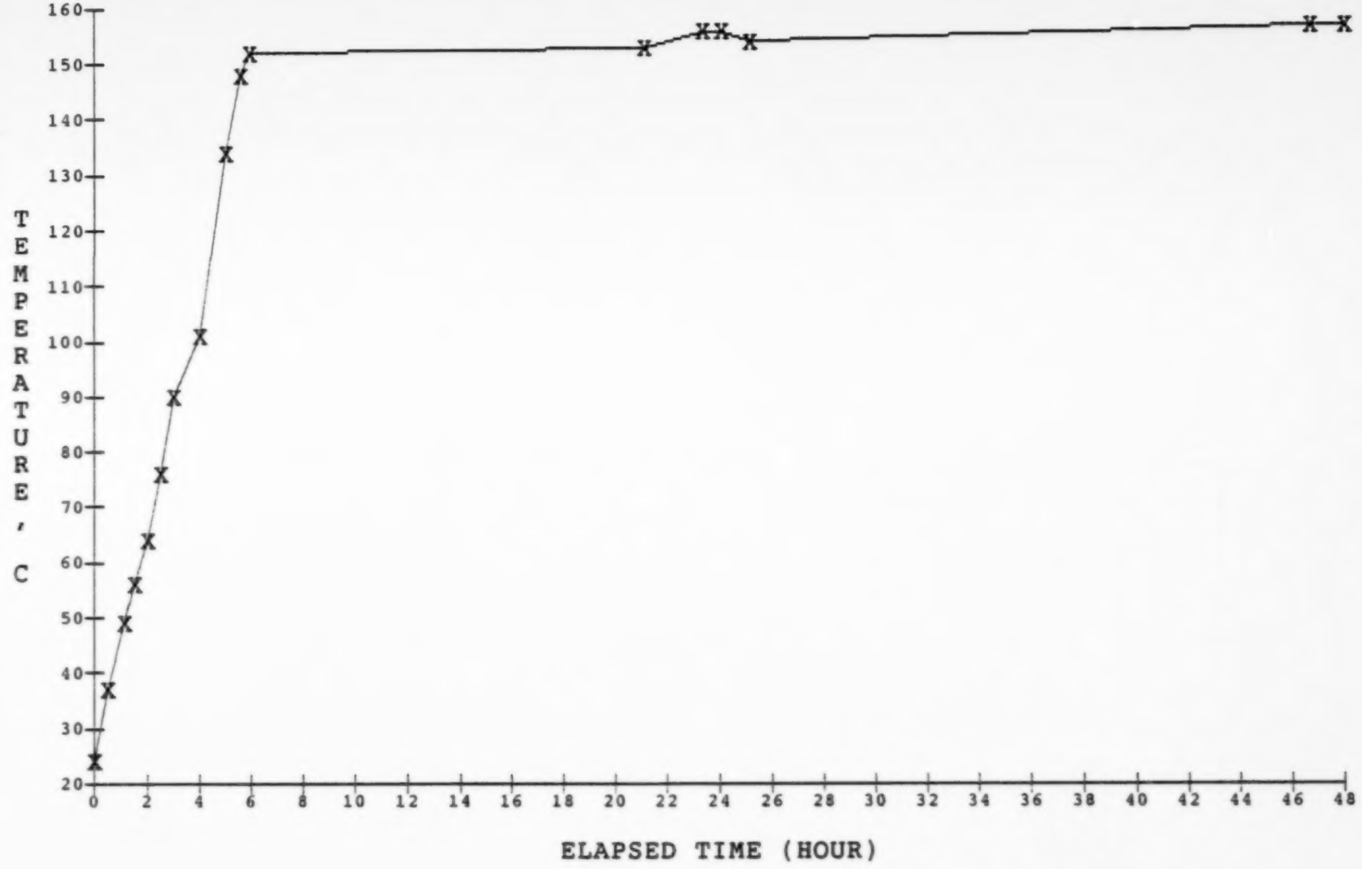


Figure 4. Temperature history for jet fuel decontamination (Experiment No. 6).

Samples of treated soil were prepared in a similar way to that of Experiments 1 through 4, described earlier.

Qualitative and quantitative results of decontamination experiments performed on soil containing jet fuel are discussed below. In the sub-section on qualitative results, the chromatograms of soil extract analysis before and after treatment are compared. In the section on quantitative results, analyses of soil for specific target compounds, total aromatics, and non-aromatics are presented.

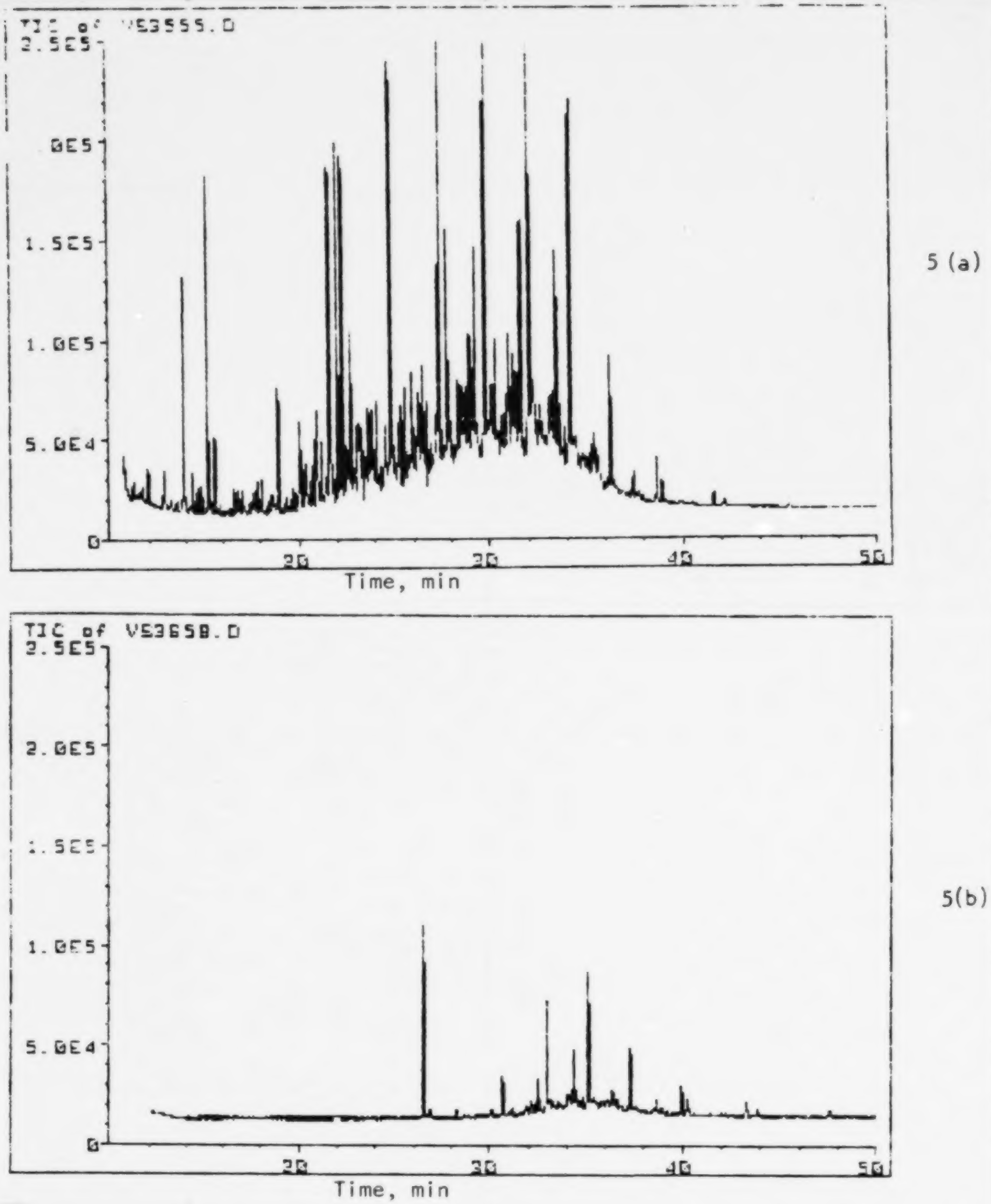
Qualitative--

The mass chromatograms for the analysis of initial and treated soil samples for Experiment 5 are shown in Figures 5(a) and 5(b). The X-axis in these figures starts at a time of 10 mins. The order of elution of the various peaks is based on the normal boiling points of the various compounds. This had occurred due to the type of capillary column used in this analysis. Thus, it is estimated that at 30 mins, compounds with a boiling point of 190°C should be eluting. Thirty-five minutes represents 220°C.

By comparing Figures 5(a) and 5(b) it can be seen that essentially complete clean-up, to the detection limit levels, was achieved for all species eluting between 10 to 27 minutes. The large peak in Figure 5b at approximately 26.5 minutes is a standard.

Similar chromatograms for Experiment 6 are presented in Figures 6(a) and 6(b). In Experiment 6, water was injected and the total soak duration was longer, compared to that of Experiment 5. In Figure 6(b), the analysis of the treated soil is shown. The first five major peaks, counting from the origin are standards.

Relative Reduction in Chromatogram Area Response--The results of Experiments 5 and 6 show that significant clean-up is feasible by heating the soil to 150°-157°C range followed by a soak period of 14 to 40 hrs. The peak areas obtained by the analysis of treated and untreated soil extracts are compared in Table 11. The results of Experiment 6 show a relative total peak area response reduction of 99%; for Experiment 5, the reduction in area response was 90%.



NOTE: X-axis starts at 10 minutes.

Figure 5. Chromatograms for Experiment 5. (a) Analysis of initial soil; (b) Soil analysis after treatment.

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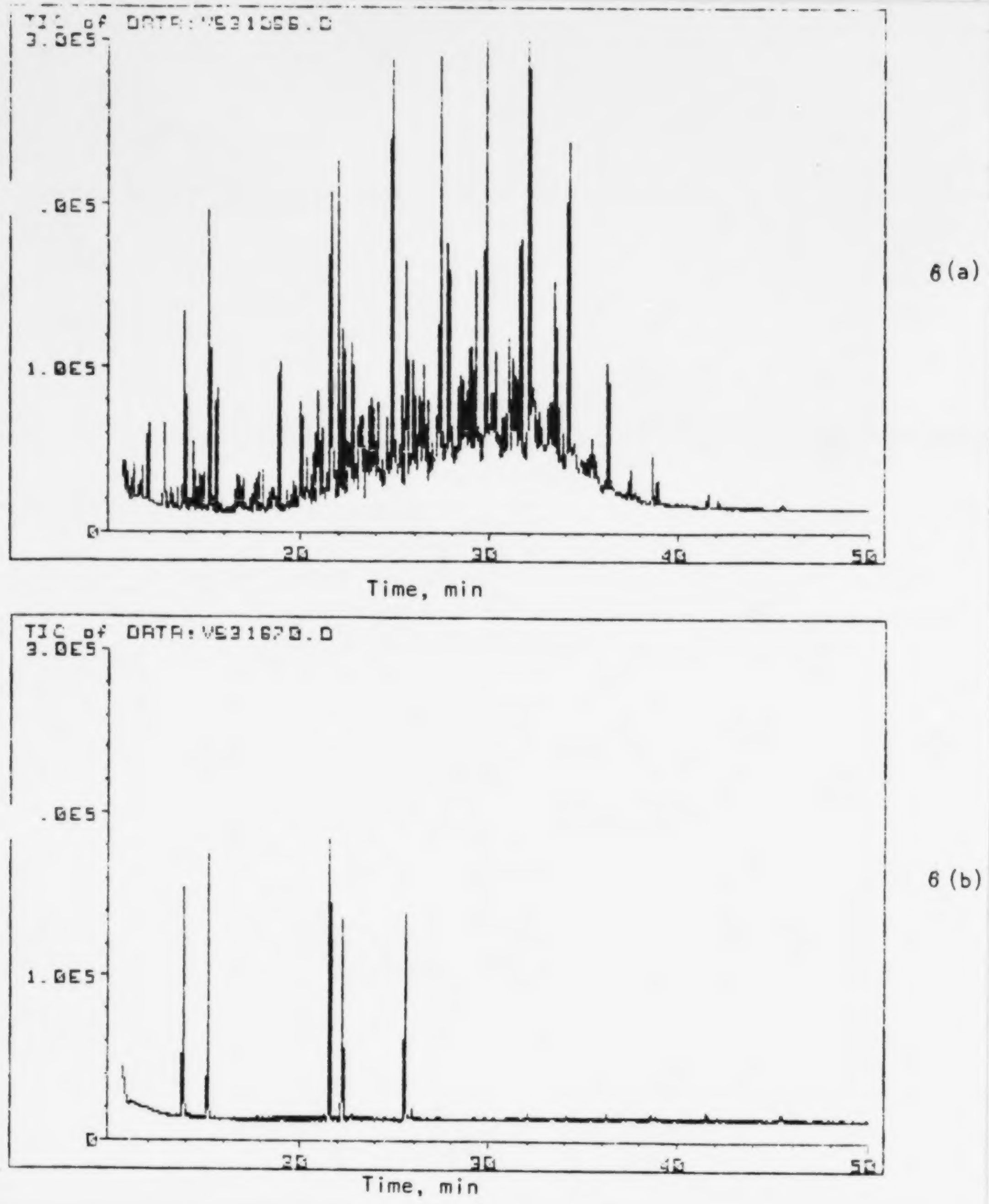

NOTE: X-axis starts at 10 minutes.

Figure 6. Chromatograms for Experiment 6. (a) Analysis of initial soil; (b) Soil analysis after treatment.

TABLE 11. COMPARISON OF TOTAL AREA RESPONSE

	Initial Soil				Treated Soil				
Exp. No.	Sample Weight, gm	Extract Volume, ml	Volume of Injection, µl	Area Response	Sample Weight, gm	Extract Volume, ml	Volume Injected, µl	Area Response	Area Reduction, %
5	151.5	100	2.0	3.52×10^8	150.3	100	2.0	0.33×10^8	91
6	150.7	100	2.0	3.92×10^8	150.6	100	2.0	0.04×10^8	99

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Quantitative Results

The concentration of toluene, pentadecane, total aromatics, and a total non-aromatics in the soil before and after treatment was determined. This was done by a GC/MS analysis of a soil extract obtained by Nielson-Kryger steam distillation. These details are given Appendix A.

In Table 12, the initial and final concentrations of each of the four measurements are compared for Experiments 5 and 6. Toluene was below the detection limit for both the soil samples of Experiment 5. It is estimated that the detection limit is approximately 3 ppm. In Experiment 6, toluene concentration was reduced from 4.3 ppm to below the detection limit.

When water is not injected, a 75% reduction of pentadecane was observed. When water is injected, pentadecane was reduced from 55 ppm to below the detection limit, a reduction of 94.5%. In both experiments, the total aromatics were reduced to BDL.

TABLE 12. BENCH-SCALE DECONTAMINATION OF SOIL CONTAINING JET FUEL (TREATMENT TEMPERATURE 150°-157°C)

In Soil	Exp. 5	Exp. 6
Steam Sweep	No	Yes
Initial Toluene, ppm	BDL[a]	4.3
Final Toluene, ppm	BDL	BDL
Initial Pentadecane, ppm	104.7	55
Final Pentadecane, ppm	25.9	BDL
Initial Total Aromatics, ppm	385	479
Final Total Aromatics, ppm	BDL	BDL
Initial Total Non-Aromatics, ppm	4871	3407
Final Non-Aromatics, ppm	480	BDL
Initial Area Response	3.52×10^8	3.92×10^8
Final Area Response	0.33×10^8	0.04×10^8
% Area Response Reduction	91	99

[a] Estimated detection limit based on iodofluorotoluene (internal standard).

4-5 kg of soil in each experiment.

Residence time at final temperature: 14 to 40 hrs.

CONCLUSIONS

The pilot-scale experiments performed with CBZ and TRCE confirmed the results obtained in the bench-scale experiments. It was shown that both the contaminants can be removed from tall columns of soil in reasonable treatment time which can be economically provided under in-situ conditions.

When a 6-ft tall column of soil containing jet fuel was subjected to thermal treatment at 152°-157°C for a period of 14 to 40 hours, the reduction in total contaminants was in the range of 90-99%. It was shown that steam sweep generated through injection of water at the bottom of the bed significantly improved the removal of higher boiling fractions in the fuel. For example, without water injection, approximately 75% removal of pentadecane was observed, with water injection the pentadecane removal was greater than 94%.

The tall column experiments have shown that in-situ heating followed by removal of vapors can be used for decontaminating soils under in-situ conditions.

IMPLICATIONS FOR IN-SITU TEST DESIGN

The pilot-scale experimental results have demonstrated that it should be feasible to decontaminate 6- to 10-ft thick beds of soil by using the in-situ heating techniques. For the Volk Field site which has JP-4 jet fuel, solvents, degreasing agents, etc. in sandy soil, a treatment temperature range of 130°-160°C should be sufficient for at least 90% decontamination.

Results on high boilers such as pentadecane indicate that water injection may be necessary to achieve 90% removal. Water can be easily injected in the in-situ field test by using selected electrodes as injection wells. Electrodes are implaced in bore holes drilled through the soil to apply RF power to the heated volume.

In the pilot-scale experiments, lateral movement of the heated contaminants was restrained by the cylindrical walls of the reactor. Under field conditions, no such physical barriers to lateral contaminant migration exist. Outward migration from the heated zone will, however, be mitigated by the presence of the cool soil surrounding the heated zone. In the cool zone, permeability to flow of gasses should be one to three orders of magnitude less than that in the heated zone, because of the presence of liquids in the pore space.

In the field-test design described in Section 11, it is proposed to place a barrier surrounding the heated test zone to isolate it against lateral migration of fluids. The design is such that it would permit estimates of the degree of migration from the heated volume.

SECTION 5

THERMAL REMOVAL OF PCB'S FROM SOILS

In this project, the feasibility of in-situ treatment of PCB-contaminated soil was evaluated by two different methods, both based on in-situ RF heating of the soil. The first method (described in this section) is based on heating the soil to a temperature range of 150°-300°C to remove the PCB's by thermal desorption/ vaporization. The second method (described in Section 6) is based on in-situ application of potassium polyethylene glycolate (KPEG) to the soil, followed by in-situ heating to promote the reaction between PCB's and KPEG, by boiling out the water and by improving reaction rates at elevated temperatures. It has been shown[4] that water in excess of 2.5% is deleterious to these reactions.

In the thermal decontamination experiments it was found that after treatment at 300°C for a period of 6 to 28 hours, there was a 99% reduction in Aroclor 1242 content of the soil. At lower treatment temperatures of 150°-200°C, 71 to 87% reduction in PCB content was observed. Mass balance on Aroclor 1242 was made for each experiment. It was observed that mass balance closure appears to be inversely related to the treatment temperature. Thus for experiments at 300°C, where 99% removal was observed, mass balance closure of 7-17% was obtained. In the lower temperature range, mass balance closure of 73-82% was obtained. The reason for these observations could not be elucidated. These results suggest that an in-situ treatment process for Aroclor 1242 can be devised, provided the fate of Aroclor 1242 at high temperature conditions is explained.

BACKGROUND AND PROBLEM DISCUSSION

Polychlorinated biphenyls (PCB's) are known to occur in many controlled and uncontrolled hazardous waste landfills and spill sites. They were utilized in transformers and capacitors because they possess excellent dielectric strength properties, thermal stability, flame retardant capability, and resistance to chemical reaction. Although manufacture and use of these chemicals was strictly regulated by EPA in 1976, PCB's continue to persist in the environment due to their stability.

Present methods for treating soil containing PCB's are largely limited to excavation of the soil followed by incineration. Various soil treatment processes are under development in which the soil is treated with polyethylene glycol alkoxides made by mixing polyethylene glycol with sodium or preferably potassium hydroxide. It was shown by Brunelle and Singleton[4] that when polyethylene glycol methyl ether (PEGM) and KOH are used for the decontamination of soils containing PCB's, poor reaction occurs with lower chlorinated PCB's such as those found in Aroclor 1242, 1016, etc. For example, it was found that only 27% of Aroclor 1242 reacted in a period of 14 days at room temperature. Aroclor 1016 showed no evidence of reaction under similar treatment conditions. It is suspected that similar results would be obtained when polyethylene glycol is used instead of PEGM. On the other hand, fairly rapid reaction rates were observed when higher chlorinated PCB's such as those found in Aroclor 1260 are present in the soil.

The thermal desorption/vaporization experiments were conducted with Aroclor 1242. In the temperature range 150°-300°C, pure Aroclor 1242 has a vapor pressure of 1.4 to 462 mmHg. Even though vapor pressure reduction should occur due to adsorption effects, nevertheless, it was anticipated that substantial vapor pressure of Aroclor 1242 would exist in this temperature range to allow fairly rapid removal of Aroclor 1242 from soil. It was the purpose of these experiments to show that this is indeed feasible.

It was also shown by Brunelle and Singleton[4] that when soils containing mixtures of lower and high chlorinated Aroclors are treated at room temperature with the PEGM/KOH reagent, the higher chlorinated species react rapidly whereas the lower chlorinated PCB's remain relatively unreacted. On the other hand, higher chlorinated PCB's such as pure Aroclor 1260 have a lower vapor pressure in the range of 150° to 300°C. For Aroclor 1260, the vapor pressure range is 0.6 to 110 mmHg. Thus, whereas the lower chlorinated PCB's might be amenable to thermal desorption/vaporization, the higher chlorinated ones should be treatable by the application of the PEG/KOH reagent. Thus, the purpose of the second method of PCB treatment was to determine whether the reaction could be carried out under in-situ conditions.

Should both methods prove feasible, then a combined process based on in-situ heating can be devised where lower chlorinated PCB's are removed by the thermal treatment while the higher chlorinated PCB's are dechlorinated in situ. Both mechanisms would work simultaneously for the in-situ treatment of a site containing mixtures of various PCB's.

In this section, the results of experiments performed to determine the feasibility of removing Aroclor 1242 from soil by thermal treatment are discussed.

EXPERIMENTAL OBJECTIVES

The two main objectives of the experiments reported in this section were: (1) to determine the feasibility of the removal of Aroclor 1242 from soil by thermal desorption assisted by steam sweep developed through water or steam injection, and (2) to demonstrate a mass balance on Aroclor 1242.

APPROACH

Several exploratory experiments were performed on spiked sandy soil. The experiments were designed to approximate in-situ treatment conditions for temperature, and method of recovery of vaporized PCB's, etc. For example, a temperature range of 200° to 300°C was selected, based on the temperatures easily attained with currently available hardware and design of the RF in-situ heating system. In all experiments, soil was packed in a column 6 to 12 in. tall and vapors were recovered from the top and bottom surfaces. No vacuum was applied. Because of the exploratory nature of the experiments a firm experimental plan was not developed, instead the results of previous experiments were used to set the operating conditions for subsequent experiments.

SPIKING OF SOIL

In all the decontamination experiments, sandy soil spiked with Aroclor 1242 was used. The soil was spiked in 1-1.5 kg batches. First, the moisture content of the clean soil was measured and adjusted to 5% wt by the addition of hydrocarbon-free water. The soil was tumbled in a glass jar to homogenize the water spike. The Aroclor 1242 spiking solution was prepared by dissolving reagent grade Aroclor 1242 in iso octane. The volume of the spiking solution necessary to give a PCB concentration of 1000 μg/gm (1000 ppm) was determined through an analysis of the spike solution on a GC equipped with an electron capture detector. After adding the spike, the glass jar was sealed and tumbled to homogenize the spike with the soil.

In addition to preparing the soil for experiments, smaller quantities of soil were spiked with diluted spiking solution to obtain soil containing 200 and 400 ppm Aroclor 1242. These samples, together with the 1000 ppm soil, were extracted to determine the recovery efficiency correction for the Soxhlet extraction procedure described in Appendix B. Soxhlet extraction of the soil was performed prior to GC/ECD analysis of soil extract to determine the residual PCB concentration after each decontamination experiments.

EXPERIMENTAL PROCEDURE

In all experiments, 200-1000 g of soil containing 1000 ppm of Aroclor 1242 was packed in a tubular stainless steel reactor. The depth of soil in these reactors varied between 6 to 12 in. depending upon the amount of soil used. The general set-up used in the experiments is illustrated in Figure 7. The upper end of the reactor was connected to a vapor recovery line leading to a "Dudley" trap where the vapors were condensed in an ice bath. The Dudley trap was vented to a Tenax® trap as shown.

The bottom of the reactor was designed such that it could be attached to a Dudley trap arrangement similar to the top or it could be terminated with a rubber septa for injecting water. Water injection was performed to provide a steam sweep to help the removal of PCB vapors from the soil towards the top of the reactor for recovery in the top Dudley trap. Prior to water injection,

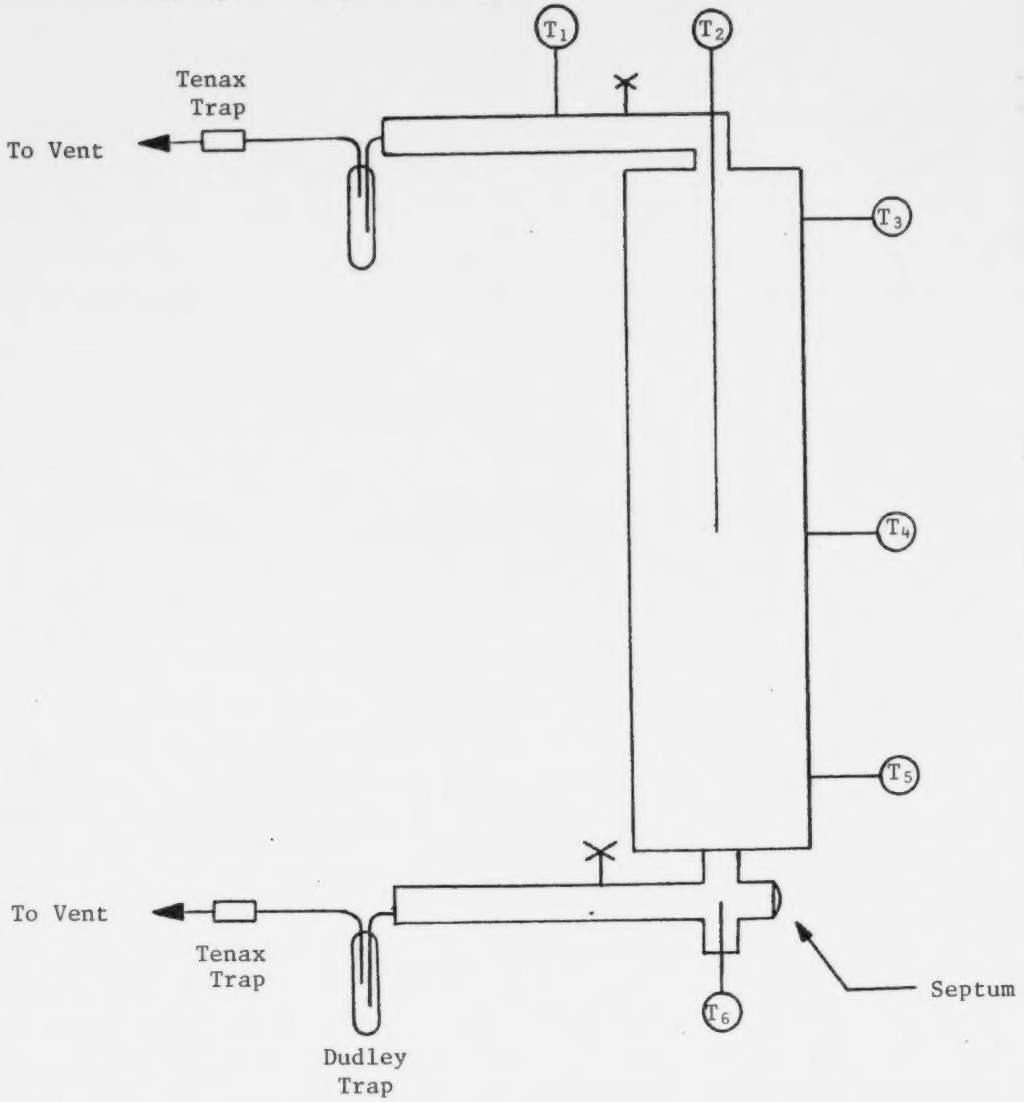
T_1
T_2
Tenax Trap
To Vent
T_3
T_4
T_5
To Vent
Tenax Trap
Septum
T_6
Dudley Trap

Figure 7. Set-up for thermal treatment of soil containing Aroclor 1242.

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the top Dudley trap was replaced so that the amount of PCB recovered due to vaporization could be separately measured from the additional amount recovered as a result of water injection.

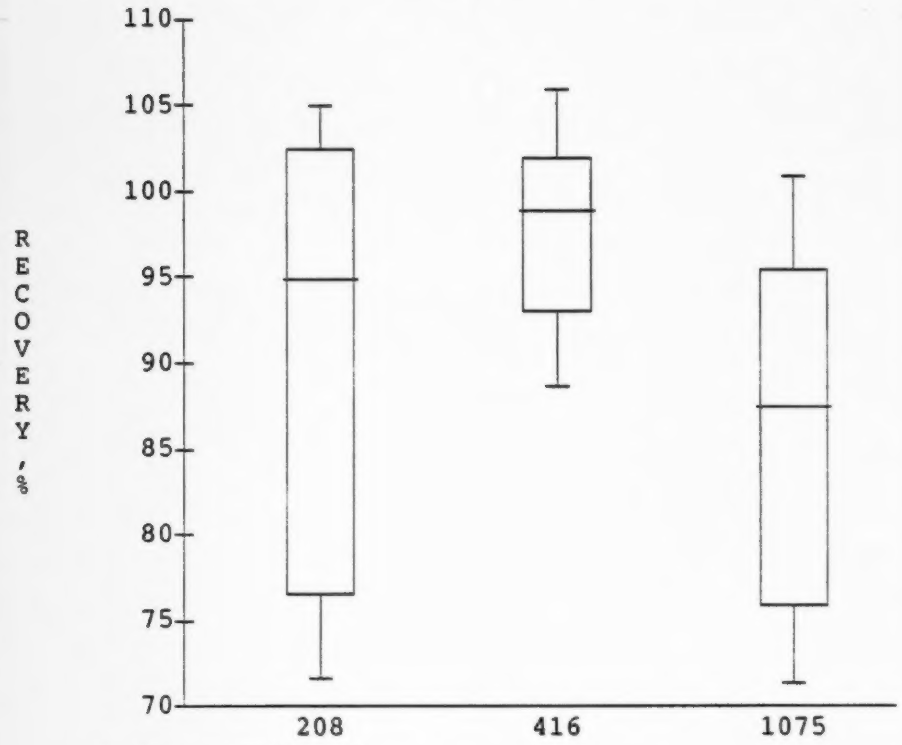
A thermocouple was placed at the approximate center of the soil bed. Several other thermocouples were placed on the outer walls of the reactor and the vapor collection tubing. Electrical heating tapes were used to heat the reactor as well as all vapor lines. Controllers were used to control the temperature at the center of the soil bed as well as the vapor lines.

PROCEDURE FOR ESTABLISHING MASS BALANCE

At the end of each experiment soil was removed from the cooled reactor, transferred to a clean glass jar and tumbled on a roller. Soil samples were taken for Soxhlet extraction with pesticide-grade hexane. The extract was analyzed to determine residual PCB concentration in soil. The PCB concentration determined by the analysis of the extract was corrected by extraction efficiency determined from repeated extractions of PCB-spiked soil. Figure 8 is a box plot showing the extraction efficiency of three different soil-spiking levels. Appendix B contains detailed information on the analytical procedures used for the analysis of Aroclor 1242.

The reactor and all tubings were rinsed with pesticide-grade hexane. The rinsate was later analyzed for Aroclor 1242. All the liquid collected in the Dudley traps was removed and saved. Most of the collected liquid was water, however, in some experiments, a small amount (one or two drops) of second phase was also visible in the traps. The recovered liquid from the traps was extracted with HPLC-grade hexane. The separated extract phase was concentrated by reducing the volume to 2 ml by nitrogen blowdown. The volume was then adjusted to 10 ml by iso-octane. The prepared extract phase and the various rinsates were analyzed for Aroclor 1242. It was assumed that the recovery efficiency of liquid-liquid extraction procedure is 100%. The detailed procedures for liquid-liquid extraction are described in Appendix B.

PCB mass balance was calculated from the following equation:



CONCENTRATION,PPM	208	416	1075
# Pts	11	11	8
Mean	92.081818	98.481818	86.2625
IQR	26	8.9	19.7

Figure 8. Box plot for Aroclor 1242 recovery efficiency by Soxhlet extraction.

Percent Mass Balance Closure =

$$\frac{\text{Mass in Treated Soil + Mass in Dudley Traps + Mass in Rinsates}}{\text{Initial Mass of PCB in Soil}}$$

In addition, percent recovery and percent removed from soil were calculated based on the following two equations:

$$\text{Percent Removal} = \frac{\text{Mass Initially Present in Soil - Residual Mass in Soil}}{\text{Mass Initially Present}}$$

$$\text{Percent Recovery} = \frac{\text{Mass in Dudley Traps + Mass in All Rinsates}}{\text{Mass Initially Present}}$$

RESULTS

Six different experiments were performed on soil containing Aroclor 1242 spike. The summary of results is presented in Table 13. The experimental conditions are summarized in Table 14 and the mass balance details are given in Table 15, from which Table 13 data were derived.

The results in Table 13 show that when the treatment temperature is 300°C, greater than 99% removal of Aroclor 1242 can be achieved. However, at the high temperature PCB mass balance is not closed. For example, in Experiments 1 and 2, mass balance closure was only 7.3 and 17.2%, respectively. Analysis of treated soil as well as the liquid collected in the Dudley traps does not account for enough PCB's to close the balance. At the end of Experiment 1, five different samples of soil were taken from the treated batch (after tumbling on a roller mill) for Soxhlet extraction. The average concentration of these five samples was 2.7 ppm ± 1.3 ppm. The range was 0.9 ppm to 4.9 ppm. This result ruled out the possibility of large errors in the mass balance due to gross non-uniformity of PCB concentration distribution in the treated soil samples. In subsequent experiments only one sample of treated, tumbled soil was analyzed to determine the residual concentration of Aroclor 1242.

After performing two experiments at 300°C, it was postulated that the inability to close the mass balance may be due to a leak in the reactor and tubing system, or due to reaction between the PCB's and the soil such that PCB

TABLE 13. AROCLOR 1242 REMOVAL FROM SOIL BY THERMAL TREATMENT

Exp. No.	Soil Wt g	Initial PCB 1242 Conc. µg/gm	Residual Conc. µg/gm	Treatment Temp. °C	Water Injected ml	PCB Removal From Soil %	PCB Recovery %	PCB Mass Balance %
1	1271	1075	2.7	250/300	None	99.8	7.04	7.3
2	1271	1039	3.6	300	20	99.7	16.9	17.2
5	211	1039	315.8	200	60	71.2	33.4	62.3
6A	206	1039	310.2	150	268*	72	54	82
4A	188	1039	138.9	150	320	87	61	73
4	205	1039	515.2**	150	53	47.8**	22	76

*Injected as steam.

**Soil was wet after experiment.

TABLE 14. EXPERIMENTAL CONDITIONS FOR THERMAL TREATMENT OF AROCLOR 1242

	Initial Soak		Water	Second Soak		
Expt. No.	Temp. °C	Time h	Inj. ml	Temp. °C	Time h	Remarks
1	250	13	None	300	15	
2	300	5.5	20	300	0.4	
5	200	17	60	200	22.3	
6A	150	0.4	268	150	.25	Water injected as steam at 150°C
4A	150	19.3	220	150	28.3	Allowed to cool down to RT for 85 hrs
4A*	150	0.5	100	150	17.2	Heating resumed after 84 hr at RT
4	150	17.3	53	160	6.0	

*Resumed

TABLE 15. AROCLOR 1242 MASS BALANCE SUMMARY

	Soil		Before Water Inj.		After Water Inj.	PCB in Rinsates	
Exp. No.	Initial Mass µg	Residual Mass µg	Water Collected g	PCB Recovery µg	PCB Recovery µg	Reactor µg	Tubing µg
1	1,365,250	3,176	98.6	96,148	None	-	-
2	1,320,570	4,230	97.2	214,180	8,500	-	-
5	219,229	63,166	10.7	12,715	60,250	73	240.1
6A	214,034	60,644	-	-	114,625	75	564.0
4A	195,332	24,794	11.2	4088	109,274	240	4,588
4	212,995	111,330	10.5	14,415	14,057	3,680	18,580

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cannot be extracted by the Soxhlet procedure. In order to rule out the possibility of leaks an experiment was performed by heating to 300°C, 34 gm of soil sealed in a stainless steel tube, which had been leak tested with nitrogen at 20 psig. The results of this experiment showed a residual concentration of 28.7 ppm, but a mass balance closure of only 19.3%. No vapors, etc. were allowed to leave the reactor during this experiment.

Having ruled out leaks as the reason for poor mass balance, additional experiments were performed at temperatures of 200° and 150°C. In the 200°C experiment, 71% removal of Aroclor 1242 and 62% mass balance closure was achieved. As the treatment temperature was dropped to 150°C, the mass balance closure increased to 73-82% (Experiments 4, 4A, 6A) while percent removal was 72-87% (Exp. 4A, 6A). In Experiment 4, the removal was only 48% but the treated soil in this experiment was found to be wet, indicating incomplete removal of water or rewetting of soil due to reverse flow of water from the trap to the reactor.

The results of these exploratory experiments show that at high temperatures, substantial removal or transformation of Aroclor 1242 occurs, such that the extractable PCB content of the soil can be reduced to 2-4 ppm after treatment at 300°C for a period of 16-44 hours. However, the poor mass balance closure indicates strong probability of either soil/PCB or PCB/stainless steel interaction.

These results show that thermal treatment of soil in the temperature range of 150°-300°C is an area that needs further investigation. The results of 300°C experiments, although very promising, have raised questions regarding the fate of the PCB's. If these questions can be answered then an economically attractive process for soil treatment based on in situ heating can be designed. Previous cost[5] evaluation studies in which mass-balance closure was assumed, have shown that the heating process would be 2 to 4 times cheaper than incineration. These studies had assumed that the treatment temperature would be in the 200°-400°C range and that the soaking time would be 14 days.

SECTION 6

IN SITU DECONTAMINATION OF SOIL CONTAINING PCB BY REACTION WITH POLYETHYLENE GLYCOL/KOH

Bench- and pre-pilot scale experiments were conducted to determine the feasibility of in-situ treatment of soil containing Aroclor 1260 by the application of potassium polyethylene glycolate. In-situ heating of the soil will be used to promote the reaction by vaporizing the moisture and improve the reaction rate. The results of these experiments are summarized below:

- when 25 gms of contaminated soil were mixed with KPEG and placed in an oven at 140°C, 99% destruction of PCB 1260 was observed in a period of 2.5 to 8 hrs
- when larger scale experiments were done, using 300 g of packed soil in a cylindrical reactor, only 16-35% destruction was observed. In these experiments, KPEG was applied to the surface of the soil bed without mixing.
- Thorough pre-mixing of soil, application of vacuum to remove moisture, use of longer treatment time (up to 72 hrs) did not help to increase the destruction efficiency in the larger scale experiments.
- It was concluded that in-situ treatment by KPEG application may not be feasible.

REAGENTS FOR PCB DECONTAMINATION

Recent studies have shown that the reaction between alkali metals or alkali metal hydroxides with polyglycols or polyglycol monoalkyl ethers provides reaction products that are capable of decontaminating a host of chlorinated hydrocarbons such as PCBs, DDT, hexachlorobenzene, trichlorobenzene etc. In particular it has been reported[2,6-10] that when the alkoxides produced by the above reactions are prepared from polyethylene glycol (PEG) of average molecular weight in the range of 350-600 or polyethylene glycol monomethyl ether (PEGM) of the similar molecular weight range, good decontamination is observed. Two types of alkali metals have been used for the preparation of the alkoxide. These are sodium and potassium. Although the elemental forms of these alkali metals may be used for producing the alkoxides, the hydroxides are safer to work with. The elemental forms produce hydrogen during the formation of the glycolates. This poses a potential safety hazard and requires special precautions to prevent fires and explosions. The reaction between sodium and polyethylene glycol proceeds with the formation of sodium glycolate and hydrogen according to the following reaction:

$$2Na + 2R\text{-}CH_2\text{-}OH \rightarrow 2R\text{-}CH_2ONa + H_2 \qquad (1)$$

If the hydroxide is used, then water is produced instead of hydrogen gas. Similar reactions occur when potassium or its hydroxide are reacted with PEG.

When the alkali metal glycolate is reacted with PCB or with a fluid containing PCB in a temperature range of 60 to 120°C the PCB molecule is dechlorinated due to nucleophilic displacement of the chlorine atoms by the alkoxide. A review of the pertinent literature reveals that there is some disagreement between the investigators on the exact mechanism of these reactions. For example, Pytlewski[2] et. al. argue that oxygen is necessary not only for the synthesis of the reagent but also for the decontamination reaction between PCBs and the reagent. On the other hand, Brunelle and Singleton[11] have demonstrated that decontamination proceeds even in the inert environment of nitrogen.

Depending upon the reaction conditions and the amount of excess base used in the reaction, various products are produced such as hydroxylated biphenyls and the sodium salt of a derivative of glycolic acid.[11]

Brunelle and Singleton[11] prepared three pure PCB isomers in order to obtain more information about the actual PCB/glycol products. When pentachlorobiphenyl was reacted with hexaethyleneglycol and KOH at ambient conditions, aryl polyglycol was detected; no phenyl was detected. When Aroclor 1260 was reacted with hexaethyleneglycol and KOH at 100°C, the aromatics containing fraction was found to be aryl polyglycols with some byphenylol.

In the feasibility experiments on decontamination of soil, the reagent was prepared by the reaction of KOH pellets (85% KOH, ACS reagent grade) with polyethyleneglycol of average molecular weight 400. For every 100 gms of the PEG 400, 16.5 gms of 85% KOH was used. This represents a molar ratio of 1:1. The reagents were mixed together in a flask, placed on a hot plate, and heated to 80°C under a nitrogen blanket. A magnetic stirrer was used to provide agitation.

BENCH-SCALE EXPERIMENTS

Bench-scale experiments were performed to determine the effect of temperature, residence time, and KPEG concentration. In all experiments 25 g of soil containing approximately 1000 ppm of Aroclor 1260 was used. The KPEG reagent was applied neat as prepared by the method described above or else applied as a solution in distilled water. The amount of KPEG applied was varied as shown in Table 16. After mixing the soil with the reagent, the soil was placed in a preheated oven. During this time soil was not mixed. At the end of the experiment, the soil was quenched with HCl to stop the reaction. Samples of soil were removed for analysis of residual PCB's according to method described in Appendix C.

The results of these experiments, presented in Table 16, show that decontamination of soil containing Aroclor 1260 is feasible. Depending upon the conditions, up to 99% destruction can be obtained in a period of 2.5 to 8.0 hrs.

In all the experiments, the quantity of KPEG used was 10 to 45 times the stoichiometric amount necessary to react with all chlorine atoms on Aroclor 1260.

PRE-PILOT SCALE SOIL DECONTAMINATION EXPERIMENTS

Decontamination experiments were performed in a tubular reactor in which 300 g of PCB contaminated soil was treated with various amounts of the KPEG reagent. The purpose of these experiments was to study the effect of residence time, treatment temperature, and percent excess KPEG on the degree

TABLE 16. BENCH-SCALE AROCLOR 1260[a] DECONTAMINATION WITH KPEG REAGENT

Expt No.	% KPEG Wet Basis	% KPEG Dry Basis	Time hr	% Water[b]	% Reaction
TR7a	6.00	13.6	1.0	55.90	65
TR11	6.00	13.6	2.5	56.00	79
TR8a	6.00	13.6	8.0	56.00	100
TR12	9.38	13.6	2.5	31.30	60
TR9a	11.54	13.6	1.0	15.40	63
TR13	11.54	13.6	2.5	15.40	58
TR10a	11.54	13.6	8.0	15.4	100
TR14	13.04	13.6	2.5	4.35	84
TR14a	13.04	13.6	2.5	4.35	99
TR5	37.00	41.7	2.5	11.40	97
TR4	38.60	41.7	2.5	7.40	99
TR3	40.50	41.7	2.5	3.00	96

[a] 1000 ppm PCB 1260 in initial soil.

[b] All experiments with 25 g of soil containing 5% initial moisture. Additional water added during the application of an aqueous solution of KPEG in water.

TABLE 17. EXPERIMENTAL PLAN FOR PRE-PILOT SCALE AROCLOR 1260 DECONTAMINATION EXPERIMENTS

Soaking Time hrs	Final Temperature °C	KPEG/PCB Molar Ratio % of Stoichiometric
2	60	500
2	60	1000
2	110	1000
2	110	500
4	110	500
4	110	1000
4	60	500
4	60	1000

of destruction of Aroclor 1260 in soil. All the experiments were performed without mixing the reagent with the soil. Instead, reagent was applied to the top surface of a 10-cm deep soil bed. The purpose of doing this was to simulate the most convenient way of KPEG application when the process is performed in situ. A full factorial experiment plan with three variables at two levels each was used. The experimental plan is shown in Table 17. The results and procedure are described below.

Experimental Procedure

About 300 gm of Aroclor 1260 spiked soil containing approximately 5% moisture was loaded in the reactor. For each experiment, the weight of soil was recorded to the nearest gram. After loading, the reactor was sealed and hooked-up to the KPEG-injection and gas-vent lines as shown in Figure 9.

The soil was heated to the final temperature of 60°C or 110°C as per the experimental plan. A thermocouple placed in the center of the soil bed was used to measure the temperature. The gas vent lines were connected to cold traps to condense and trap moisture. The traps were placed in a cold bath consisting of dry ice and methanol. For each experiment, preweighed, dried and clean traps were used. At the end of the experiments, the traps were weighed and the condensate was transferred to sample vials and capped.

A solution of KPEG in water was prepared and placed in a preweighed flask. This solution was preheated in a water bath. A nitrogen blanket was placed on the flask. When the soil in the heated reactor had attained the desired final temperature, the KPEG pump was turned on and the reagent was injected into the reactor. After injection the flask was removed from the water bath and weighed to determine the quantity of KPEG solution injected. The pump was allowed to continue to run after removing the KPEG flask in order to empty the KPEG transfer lines by pumping residual KPEG into the reactor.

After KPEG injection was completed the reactor temperature was allowed to restabilize at the desired final temperature and soaked for a period of 2 to 4 hours as specified in the experimental plan.

The above scheme of injecting KPEG in a preloaded reactor was used only for eight runs. In the later runs the desired quantity of KPEG/water solution

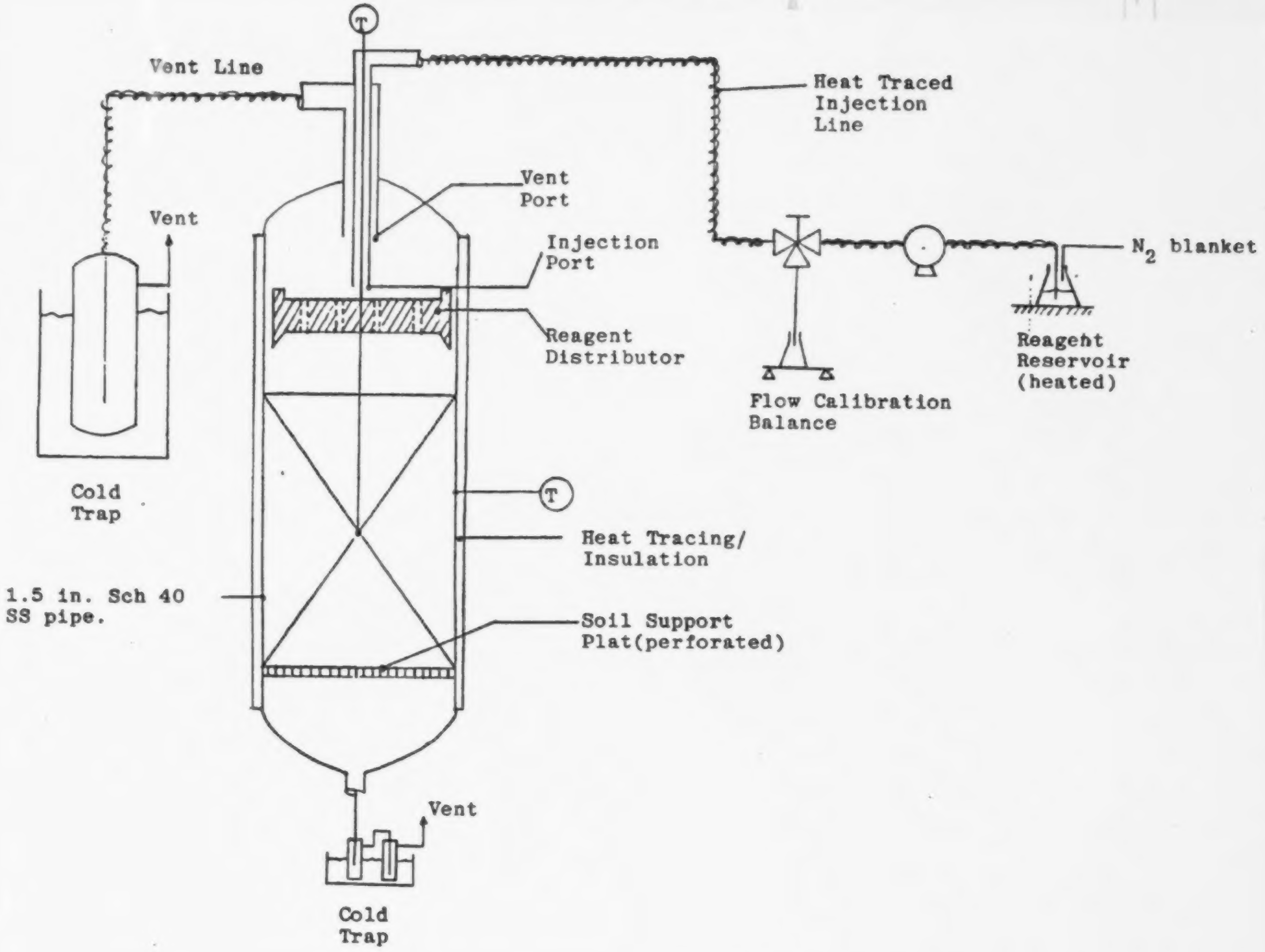
Vent Line
Vent
Cold Trap
Vent Port
Injection Port
Reagent Distributor
Heat Traced Injection Line
N$_2$ blanket
Flow Calibration Balance
Reagent Reservoir (heated)
T
Heat Tracing/ Insulation
1.5 in. Sch 40 SS pipe.
Soil Support Plat(perforated)
Vent
Cold Trap

Figure 9. Pre-pilot scale experimental set-up for Aroclor 1260 treatment.

was thoroughly premixed with the soil at room temperature. The reactor was then loaded with the mixture which was then heated up to the desired final temperature.

Results of Pre-Pilot Scale Experiments

The results of experiments performed in the reactor with 300 g of soil are shown in Table 18. Altogether 14 experiments were performed in order to investigate the effect of temperature, residence time, water content etc. The results of these experiments are discussed below.

Experiments C_1 and C_2 were performed as blanks. In experiment C_1 contaminated soil was heated to 110°C in the presence of polyethylene glycol with average molecular weight of 400. At the end of 4 hr, heating was terminated, the reactor cooled with chilled gaseous N_2 and the soil was analyzed for Aroclor 1260. After correcting for extraction efficiency there was 13% apparent destruction. In experiment C_2 contaminated soil was placed in the reactor and heated for 4 hrs at 110°C. After correcting for extraction efficiency there was an apparent destruction of 15%. In subsequent experiments C_3 through C_{14} corrections were made to the apparent destruction to obtain a corrected destruction efficiency. These corrections were made based on the results of experiments C_1 and C_2.

Experiments C_3 through C_8 in Table 18 represent conditions from the experimental plan presented in Table 17, lines 1 through 6 except with one deviation. At the time the experimental plan was devised, we envisioned using pure KPEG at concentration levels representing 5 times and 10 times the stoichiometric amounts necessary for reaction with Aroclor 1260. However, it was realized that good penetration and dispersion of KPEG in the soil would require addition of a solvent to reduce the viscosity of KPEG. We decided to use a solution of KPEG in water. However, the KPEG concentration in the injected solution was adjusted to achieve 5 times or 10 times the molar concentration requirements. At this time it was decided to keep the total quantity of the injected solution the same for all the experiments in order to avoid dispersion effects confounding the results. In Table 18, experiments

TABLE 18. SUMMARY OF REACTION CONDITIONS AND PERCENT DESTRUCTION IN THE REACTOR

Run No.	Wt. of Soil* gm	Wt. of KPEG solution gm	Conc. of KPEG solution %, wt.	Time to Reach 100°C min	Time at 100°C min	Time† to Reach Final Temp. min	Time at Final Temp. hr	Initial Temp. °C	Final Temp. °C	Destruction		Water Balance			Remarks
										Apparent %	Corrected %	Initial gm	Collected gm	Uncollected gm	
C_1	300	40	10% PEG	105	13	-	4	20	110	13	-	-	-	-	Contaminated soil + PEG solution
C_2	300	0	-	105	13	-	4	20	110	15	-	-	-	-	Blank run with contaminated soil
C_3	300	87	25	-	-	128	2	21	60	14.8	0	80	24	56	KPEG solution injected at 60°C
C_4	300	87	50	-	-	135	2	20	60	9.5	0	59	9	50	KPEG solution injected at 60°C
C_5	300	79	50	47	44	20	2	20	110	43.8	34.7	55	51	4	KPEG solution injected at R.T.
C_6	300	77	25	45	92	39	2	20	110	19.4	6.4	73	59	14	KPEG solution injected at R.T.
C_7	300	79	25	68	117	-	4	18	110	9.9	0	74	63	11	KPEG solution injected at R.T.
C_8	300	87	50	42	107	35	4	18	110	14.7	0	59	47	12	KPEG solution injected at R.T.
C_9	300	87	50	54	33	29	2	21	140	12.0	0	59	48	11	KPEG solution injected at R.T.
C_{10}	300	87	50	48	36	22	4	22	140	28	16.4	58	23	35	KPEG solution injected at R.T.
C_{11}	300	85	55	38	11	11	2	20	140	39.6	30.0	53	47	6	KPEG/soil premixed
C_{12}	300	87	50	-	-	66	2	22	140	5.2	0	59	30	29	Premixed, vacuum
C_{13}	300	88	50	30	44	20	72	22	140	43.9	34.7	59	52	7	Premixed
C_{14}	298	87	50	-	-	120	2	23	140	13.6	0	59	57	2	Premixed, vacuum

* Runs C_1 through C_8 were done with soil containing 1052 ppm Aroclor 1260; In runs C_9 through C_{14} soil was spiked with 999 ppm of PCBs.

† Time to reach final temperature from 100°C in runs where Final Temperature was greater than 100°C.

performed with 25% solution of KPEG had 5 times the stoichiometric amount of the reagent while those with 50% solution had 10 times the stoichiometric amount.

In experiments C_3 through C_8 apparent destruction efficiencies of 10 to 44% were obtained. The corrected destruction efficiency however ranged from 0 to 35%. From the data obtained there appears to be a inverse relationship between the destruction efficiency and the fraction of water not removed from the soil during the heating period. The three columns under the heading "Water Balance" in Table 18 provide information on the fate of water. It was observed that in those experiments where most of the water was removed by boiling, a higher degree of destruction was observed. Further it was observed that the amount of water boiled and recovered was not reproducible, nor was the decontamination of the soil.

In order to determine the reason for relatively low destruction efficiency of the reactor experiments, the following steps were taken:

- Runs at 60°C were discontinued. Runs were performed only above the normal boiling point of water.
- KPEG injection in preheated soil was replaced by injection at room temperature to allow maximum time for KPEG to permeate through the soil.
- KPEG injection step was replaced with premixing the soil with the KPEG solution prior to loading the reactor.
- In an attempt to improve water recovery, reaction temperature was increased to 140°C.
- To conclusively establish whether water has a deleterious effect, runs were performed under vacuum to remove the soil moisture.
- To determine whether longer residence time could off-set the effect of water, one run was performed at 140°C for a period of 72 hours.

The following conclusions were made based on the result summarized in Table 18.

- Aroclor 1260 in soil can be decontaminated by using the KPEG reagent provided at least 90% of the water can be boiled out. This corresponds to residual soil moisture concentration of less than 2.3% on a KPEG free basis.

- The system does not permit complete water removal despite heat tracing of the vent lines and of the reactor. The temperature profile in the upper half the soil bed was measured in one of the runs and found to be uniform. No cold spots were observed. The lower half could not be examined due to inadequate thermocouple length.

- The vacuum run (C_{14}) removed 97% of the water. Karl-Fisher analysis of the soil after the experiment showed 0.6% moisture, which is consistent with the water recovery obtained in this run. However, even in this case poor decontamination was observed.

- Presence of air or oxygen may be necessary for the reaction. This is indicated by the results of the two vacuum runs.

A comparison of the results obtained from the runs performed in the oven and the reactor indicates one or more of the following reasons for the low destruction observed in the reactor:

- inadequate mixing of the KPEG solution and the soil
- interferences caused by water
- lack of oxygen or air in the reactor

Based on the data obtained so far it would appear that the water content in the reaction mixture should be low, probably less than a few percent. However, the vacuum run, in which the moisture content was 0.6% indicates that presence of air or oxygen may be necessary for the reaction to occur. It should be noted however, that Brunelle and Singleton[11] performed decontamination experiments under a nitrogen blanket and observed 36 to 100% destruction. But they were working with liquid systems containing organic solvents with no water. However, when these researchers performed experiments on soil, they found that up to 2% water in the soil-reagent mixture has no deleterious effect on the reaction. But when the water content is increased from 2.5 to 10%, the water has a significant deleterious effect. Their work was done in loosely-covered containers at room temperature so the effect of excluding oxygen or air cannot be determined.

Based on the results obtained so far, it would appear that in situ treatment of soil by the application of KPEG and in the absence of mixing may not be feasible.

Additional experiments to evaluate the effect of reaction atmosphere should be performed before making a firm conclusion. This is so because in all the 300-g experiments, elimination of air could have occurred due to flow of steam as it escaped into a cold trap to which the reactor was vented.

SECTION 7

BASICS OF RADIO FREQUENCY DIELECTRIC HEATING

BASIC THEORY

The term radio frequency (RF) generally refers to the frequencies used in wireless communications. These frequencies can be as low as 45 Hz (submarine communication systems) or extend well above 10 GHz (satellite communication systems). The frequencies primarily used for radio frequency, dielectric, or microwave heating range from 6.78 MHz to 2.45 GHz.

The exact frequencies chosen for heating a particular object partially depend on the object's size and its electromagnetic (EM) characteristics. As a general rule, the higher the operating frequency, the more readily the material will absorb the energy. Too rapid an absorption, however, can cause most of the energy to be absorbed near the source of the applicator at the expense of not heating the material further away. This effect can be lessened with lower operating frequencies. Since less power is absorbed near the source, better penetration results. There is a limit, however, to which the frequency can be decreased. Since the absorbing properties drop off with frequency, a reduced heating rate will result unless the amplitude of the EM fields is increased. The amplitude, however, can be increased only up to a certain point before corona discharge, spark-over, or electrical breakdown seriously affect the operation. Thus, the precise frequency of operation would ideally be determined by the geometry of the volume and the electrical parameters of the material.

In a practical sense, other limiting factors include frequency authorization and power source availability. The industrial, scientific, and medical (ISM) band frequency channels allocated for the dielectric heating process are 6.78, 13.56, 27.12, 40.68, 915, and 2,450 MHz. Because of the wide use of dielectric heating, relatively inexpensive tubes for power sources at the ISM band frequencies are available. Therefore, selection of an ISM band frequency as the operating frequency is preferred.

When materials are placed in a conventional microwave oven and the oven is energized, the materials will absorb energy from the applied microwave electromagnetic fields. This, in turn, generates heat and raises the temperature of the material. A variety of phenomena can be responsible for this absorption of energy and subsequent heating of the material, but for purposes of designing a soil heating system, only two principal mechanisms need be considered. These are ohmic and dielectric heating.

Ohmic heating arises from an ionic current or conduction current that flows in the material in response to the applied electric field. This is similar to the current that flows in a light bulb or in resistive heating elements. Dielectric heating results from the physical or mechanical distortion of the molecular structure of the material in response to an applied electric field. Since the applied AC electric field changes rapidly, the alternating physical distortion or mechanical energy is translated into thermal energy in the material. Consequently, a portion of the energy in the electric field is converted into thermal energy in the material, creating heat and increasing the temperature.

With dielectric heating, materials whose molecular structure is readily distorted by the applied electric field are most easily heated. Molecules of this type are called polar molecules. Water is one such polar molecule. Many materials, such as plastics and ceramics, are essentially non-polar. Such materials, for a given electric field, do not heat as readily as materials composed of polar molecules.

Since water is a principal constituent of the soil, and since it is both a polar molecule and an electrolyte, its presence or absence has been found to dominate the dielectric behavior of the soil. Furthermore, it appears that the soil is a heterogeneous dielectric, composed of water molecules in the interstitial spaces of a lower-loss dielectric matrix. Such a matrix exhibits a high ability to absorb electromagnetic energy when moist, but very little ability under similar electric field conditions after the water is removed.

In theory, it is not always possible to determine which heating mechanism, ionic or dielectric, dominates in soil since some ionic current will always be flowing because of the moisture. Such microscopic phenomena are not important in evaluating the electromagnetic heating properties of materials. For example, both phenomena are generally considered in the power dissipation relationships as given in Equation (1):

$$P = \omega \varepsilon_o \varepsilon_r \tan \delta \, (E_{rms})^2 \tag{1}$$

where P = the power absorbed (W/m^3)

ω = angular frequency = $2\pi f$

f = the frequency of the applied electric field (Hz)

ε_r = the relative dielectric constant for a given frequency, f

$\tan \delta$ = the loss tangent for a given frequency, f

ε_o = permittivity of free space = 8.85×10^{-12} (F/m)

E_{rms} = rms value of the applied electric field (Volts)

The loss tangent is defined as:

$$\tan \delta = \sigma / \omega \varepsilon_o \varepsilon_r = 1 / \rho \omega \varepsilon_o \varepsilon_r \tag{2}$$

where σ = the apparent bulk conductivity of the material at frequency, f

ρ = the apparent bulk resistivity of the material at frequency, f

Substituting Equation (2) into Equation (1) yields,

$$P = \sigma (E_{rms})^2 = (E_{rms})^2 / \rho \tag{3}$$

$$P = V^2/R \tag{4}$$

Equation (1) gives a general definition for power absorbed per cubic meter for dielectric heating. It considers both the contributions from ohmic heating as well as the dielectric absorption mechanisms. This equation can be simplified into a more intuitive form as shown in Equation (3). This equation is analogous to the standard ohmic heating relationship as shown in Equation (4), where V is the applied voltage across a resistor R. The conductivity and resistivity used in Equation (3) are both functions of the applied frequency.

Also of interest in the design of a soil heating system is the depth of penetration or skin depth of the electromagnetic wave as it enters the volume of material to be heated. The skin depth is defined as the depth at which the initial amplitude of the EM wave falls to 1/e (where e ≈ 2.7183) within the material or about 37 percent of its initial value. Thus, skin depth is a measure of the penetration of the electromagnetic energy into the medium. Relationships for the skin depth of a material are given in Equations (5), (6), and (7).

$$\Delta^{-1} = \omega \left\{\frac{\mu_o \varepsilon}{2} \left[(1 + \tan^2 \delta)^{1/2} - 1\right]\right\}^{1/2} \qquad (5)$$

where Δ = the skin depth (meters)

μ_o = the permeability of free space = $4 \pi \times 10^{-7}$ (H/m)

ε = the permittivity of the material and = $\varepsilon_o \varepsilon_r$

This equation can be simplified for moist soils, where $\sigma >> \omega\varepsilon$ to:

$$\Delta \cong (\pi f \mu_o \sigma)^{-1/2} \qquad (6)$$

For dry soils, we employ the relationship for lossy dielectrics, ($\sigma << \omega\varepsilon$) so that:

$$\Delta \cong 2/(\omega \sqrt{\mu_o \varepsilon} \tan \delta) \qquad (7)$$

or

$$\Delta \cong 2(\varepsilon/\mu_o)^{1/2}/\sigma \qquad (8)$$

Another design factor is the wavelength, λ, of the electromagnetic energy in the soil. For easily designed EM energy applicators, $\lambda/2$ should be large compared to at least two dimensions of the applicator arrangement.

The wavelength of the EM field in the soil varies according to the dielectric parameters as follows:

$$\lambda^{-1} = \frac{\omega}{2\pi} \sqrt{\frac{\mu_o \varepsilon}{2} \sqrt{(1 + \tan^2 \delta)}} \qquad (9)$$

For moist soil:

$$\lambda^{-1} \cong \frac{1}{2\pi} \left(\frac{\omega\mu_o\sigma}{2}\right)^{1/2} \qquad (10)$$

For dry soil:

$$\lambda^{-1} \cong \frac{\omega}{2\pi} \sqrt{\mu_o\varepsilon \left(1 + \frac{1}{8} \tan^2 \delta\right)} \qquad (11)$$

The ability of the electric field to cause breakdown or an arc through the soil limits the maximum heating rate at a given frequency. Typically, the maximum operating electric field intensity is chosen to be no greater than one-third of the breakdown electric field intensity. Experience with oil shale and tar sand indicates that such effects do not become catastrophic until earth temperatures exceed 200°C, the temperature where pyrolysis begins dramatically.

In summary, the key dielectric parameters (relative dielectric constant, loss tangent, and conductivity) as a function of frequency and temperature in conjunction with the geometry of the material determine the appropriate selection of operating frequency and applicator dimensions for a specific dielectric heating application. Subsequently, the maximum allowable heating rate and the efficiency of energy distribution within the material are determined.

SECTION 8

MEASUREMENT OF DIELECTRIC PARAMETERS

BACKGROUND

The complex dielectric constant is defined as:

$$\varepsilon^* = \varepsilon_o(\varepsilon_r - j\frac{\sigma}{\omega\varepsilon_o}) \qquad (12)$$

where ε^* = complex dielectric constant at a given frequency, f

$j = \sqrt{-1}$

The relative dielectric constant, ε_r, is associated with the ability of the dielectric material to store electrical energy. The expression $\sigma/\omega\varepsilon_o$ is associated with the dielectric losses in the material. When σ is large the material is a good conductor of electricity; when σ is small the material is an insulator.

The loss tangent of a dielectric is defined as:

$$\tan\delta = \frac{\sigma}{\omega\varepsilon_o\varepsilon_r} \qquad (13)$$

The loss tangent is proportional to the ratio of the power lost in the material through heating to the energy stored in the material per cycle and is therefore, a measure of how "lossy" a dielectric material is.

The dielectric properties of soil are not independent of frequency and are constant only over relatively small portions of the frequency spectrum. In addition, ε^* can be noticeably affected by moisture content and temperature; therefore, to determine the dielectric properties of soil it is necessary to measure ε^* over a range of frequencies and temperatures.

PARAMETER MEASUREMENT PROCEDURE

The dielectric properties of soil samples obtained from Volk Field ANGB were measured by placing the material inside a coaxial transmission line sample holder and measuring the complex input impedance at the front of the line. The sample holder allowed for measurement of the input impedance over a frequency range of 0.5 to 20.0 MHz for sample temperatures up to 250°C. Calculation of the dielectric parameters of the material under test using this sample holder were valid for those materials whose permittivities were in the intermediate to low range. This corresponds to soils with lower concentration of water. Figure 10 is a schematic cross section view of this low frequency, low permittivity sample holder and is divided into three regions. Regions 1 and 2 are modeled using the equation for the capacitance between two cylindrical conductors.

$$C = \frac{2\pi l \varepsilon^*}{\ln(b/a)} \qquad (14)$$

where $\varepsilon^* = \varepsilon_o(\varepsilon_r - j\frac{\sigma}{\omega\varepsilon_o})$, from Eq. 12

Because of its complex geometry, the capacitance of Region 3 was determined experimentally. The capacitance of Region 3 can be expressed as,

$$C = K\varepsilon^* \qquad (15)$$

where K = a constant that depends only on the geometry of Region 3

By combining the above two equations, the total capacitance of the sample holder is,

$$C = \frac{2\pi l_1 \varepsilon_o}{\ln(b/a)} + \frac{2\pi l_2 \varepsilon^*}{\ln(b/a)} + K\varepsilon^* \qquad (16)$$

Here it is assumed that Region 1 is air-filled and Regions 2 and 3 are filled with a homogeneous dielectric of dielectric permittivity ε^*.

To determine K, a value for l_3 is selected such that AA' lies in the region of the test fixture where the standard equation for the capacitance

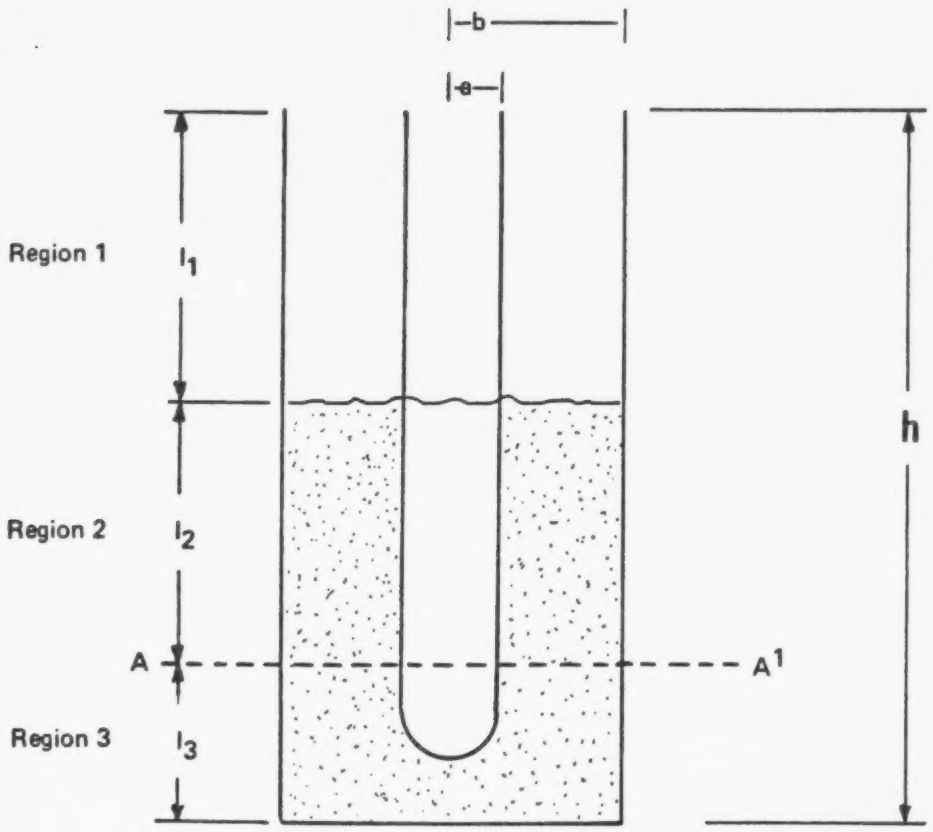
b
e
Region 1
l_1
Region 2
l_2
A
A^1
Region 3
l_3
h

Figure 10. Schematic cross-section of low frequency, low permittivity sample holder.

between two cylindrical conductors is valid. The impedance of the empty test fixture, Z_e, is measured. The total capacitance of the empty sample holder can then be written as,

$$C = \frac{1}{j\omega Z_e} = \frac{2\pi\varepsilon_o(h - l_3)}{\ln (b/a)} + K\ \varepsilon_o \tag{17}$$

where h = the height of the sample holder.

Solving for K yields,

$$K = \frac{1}{j\omega\varepsilon_o Ze} - \frac{2\pi(h - l_3)}{\ln (b/a)} \tag{18}$$

Inserting this expression into the equation for the total capacitance of the filled sample holder yields,

$$C = \frac{1}{j\omega Zr} = \frac{2\pi l_1 \varepsilon_0}{\ln (b/a)} + \frac{2\pi l_2 \varepsilon^*}{\ln (b/a)} + \left[\frac{1}{j\omega\varepsilon_0 Z_e} - \frac{2\pi(h-l_3)}{\ln (b/a)}\right]\varepsilon^* \tag{19}$$

where Zr = the measured impedance when Regions 2 and 3 are
filled with the material under test

Solving for ε^* yields,

$$\varepsilon^* = \frac{1/j\omega Zr - 2\pi\varepsilon_o l_1/\ln(b/a)}{1/j\omega\varepsilon_o Z_e - 2\pi/\ln(b/a)(h - l_2 - l_3)} \tag{20}$$

But since $h - l_2 - l_3 = l_1$ and $\varepsilon^* = \varepsilon_o(\varepsilon_r - j\ \sigma/\omega\varepsilon_o)$ this equation can be rewritten as,

$$\varepsilon_r - j\ \sigma/\omega\varepsilon_o = \frac{1/j\omega\varepsilon_o Zr - 2\pi l_1/\ln (b/a)}{1/j\omega\varepsilon_o Z_e - 2\pi l_1/\ln (b/a)} \tag{21}$$

The dielectric parameter unfold directly from Equation 21 as

$$\varepsilon_r = \text{Real part of [RHS of Eq. 21]} \tag{22}$$

$$\tan\delta = \text{Imaginary part of [RHS of Eq. 21]/Real Part of [RHS of Eq. 21]} \tag{23}$$

$$\sigma = \omega\varepsilon_o\ \text{Imaginary part of [RHS of Eq. 21]} \tag{24}$$

where RHS = right hand side.

Figure 11 illustrates the basic measurement arrangement used to measure the dielectric parameters of the soil samples. Figure 12 shows a photograph of equipment used. Illustrated in the figure are the Hewlett-Packard HP4192A low frequency impedance analyzer and HP4193A vector impedance meter. The low frequency, low-permittivity sample holder is also shown.

Heat tape was wrapped around the outside of the sample holder line to vary the temperature of the test materials. The materials were heated from room temperature to about 250°C over 4 to 4 1/2 hours and the complex input impedance recorded for selected frequencies every 5 minutes.

SOIL SAMPLES TESTED

The dielectric parameters of three sandy soil samples obtained from Volk Field ANGB Camp Douglas, WI were measured using the above procedure. Each test was performed on a small sample of approximately 200 grams of soil packed within the low frequency, low permittivity sample holder to a density as close to field conditions as possible.

Sample #1 was taken from clean sandy soil shipped to IITRI from Volk Field. Samples #2 and #3 were obtained by IITRI sampling conducted at the Fire Training Pit at Volk Field. The samples were gathered from depths of 42" to 46" in. and 84" to 89" in., respectively.

MEASUREMENT RESULTS

Three samples were tested and the dielectric parameters were calculated for the five selected frequencies of 0.5, 1.0, 5.0, 10.0, and 20.0 MHz. All three of the samples tested were heated from 25° to 250°C while using the low-frequency, low-permittivity sample holder.

The impedance data obtained were analyzed using the procedures discussed above to yield the RF dielectric parameters; relative permittivity, loss tangent, and conductivity as functions of frequency and temperature for each of the samples. Bimonthly Progress Reports #2 and #4 of this project contain the detailed results of these analyses, along with the temperature profile used for each sample run.

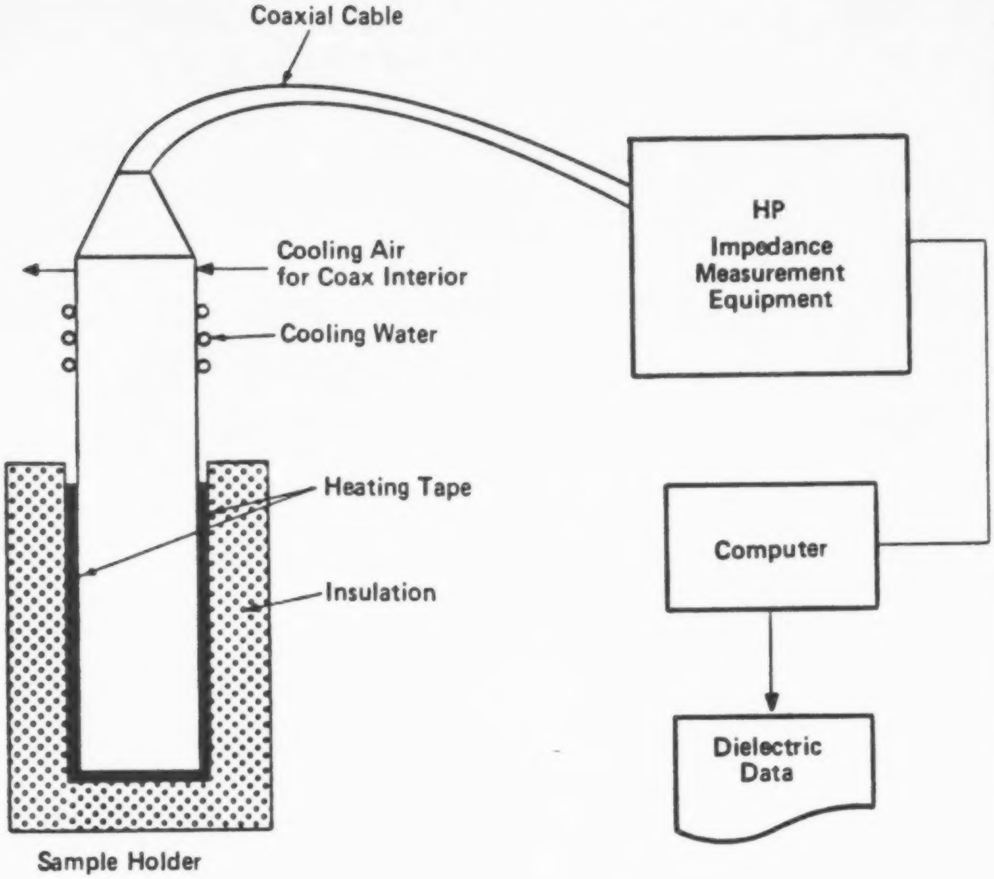
Coaxial Cable
HP
Impedance
Measurement
Equipment
Cooling Air
for Coax Interior
Cooling Water
Heating Tape
Insulation
Computer
Dielectric
Data
Sample Holder

Figure 11. Equipment set-up for the measurement of soil dielectric parameters.

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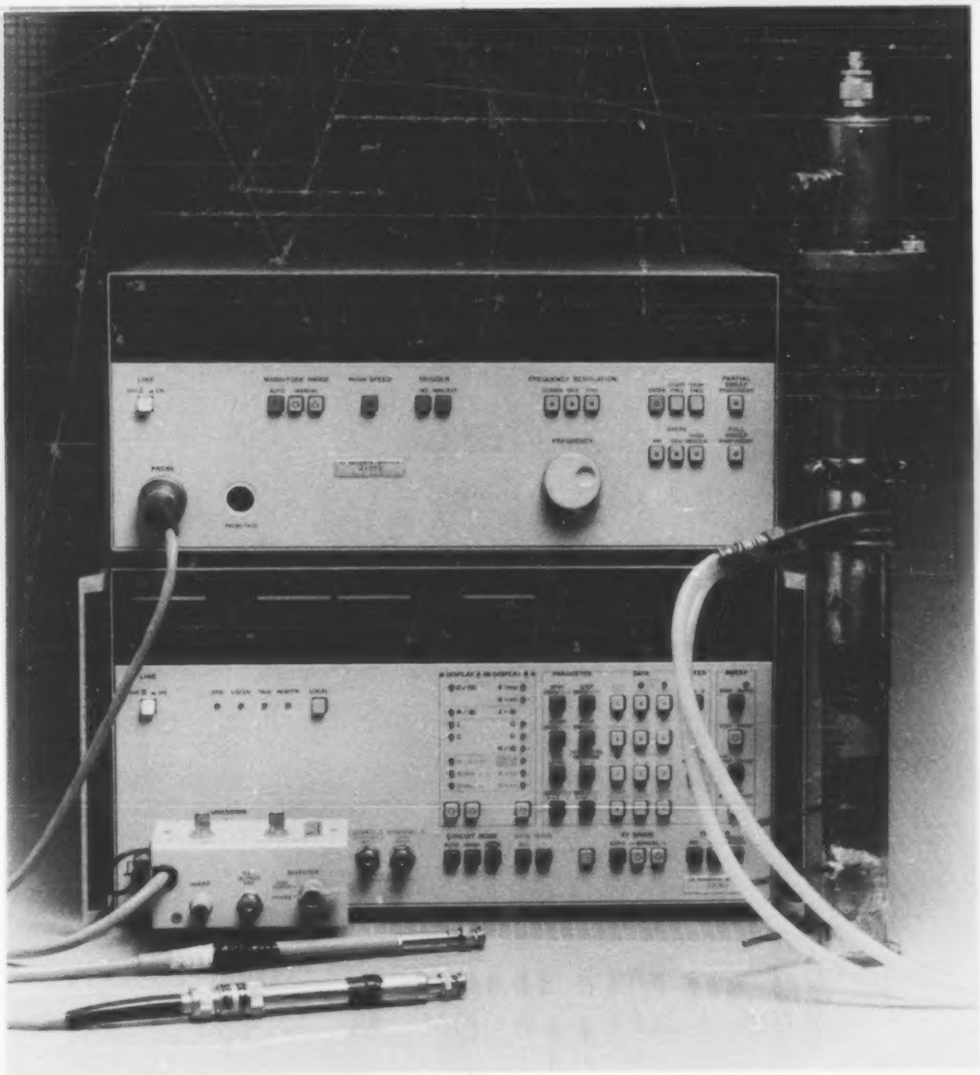

Figure 12. Photograph of soil dielectric parameter measurement instrumentation.

Figures 13 through 15 illustrate representatively the relative permittivity, loss tangent, and conductivity, respectively, as functions of temperature and frequency for soil Sample #3. All samples were held at a temperature of approximately 105°C for a period of one hour to provide ample time for the vaporization and removal of the water within the sample.

All of the dielectric parameter curves, illustrated in Figures 13 through 15 have the same rapid decrease or "roll-off" beginning after the temperature has reached 110° to 115°C. This corresponds to the water in the soil being vaporized and allowed to escape. The data obtained from Sample #2 was essentially the same as that for Sample #3 showing little or no difference in dielectric parameters for the two depths sampled. The analysis of Sample #1, the clean soil, however, indicated much lower values for the loss tangent and conductivity for all frequencies as compared to Samples #2 and #3. From the data presented on Sample #3, it can be determined that at temperatures of 150° to 160°C, the soil will be absorbing a small percentage of the power absorbed during the water vaporization phase. The power absorbed at 150°C in contaminated soil is significantly greater than in the clean soil.

The ability of the dielectric material to withstand the high intensity electric fields that will exist within the electrode array and at its edges was evaluated by conducting a dielectric breakdown test on approximately 200 grams of the Volk Field clean soil (Sample #1). The results of this test, although qualitative, indicate that for the maximum applied power densities planned for the field tests (approximately 2.5 kW/m^3), no dielectric breakdown is anticipated. During the breakdown test, as the moisture was evaporated from the soil sample, the impedance of the sample load increased significantly so as to make matching difficult. At the termination of the test, approximately 95% of the moisture had been evaporated. RF energy, although only a few percent of that applied from the source, was still being absorbed by the soil sample load as noted by the continuing temperature increase.

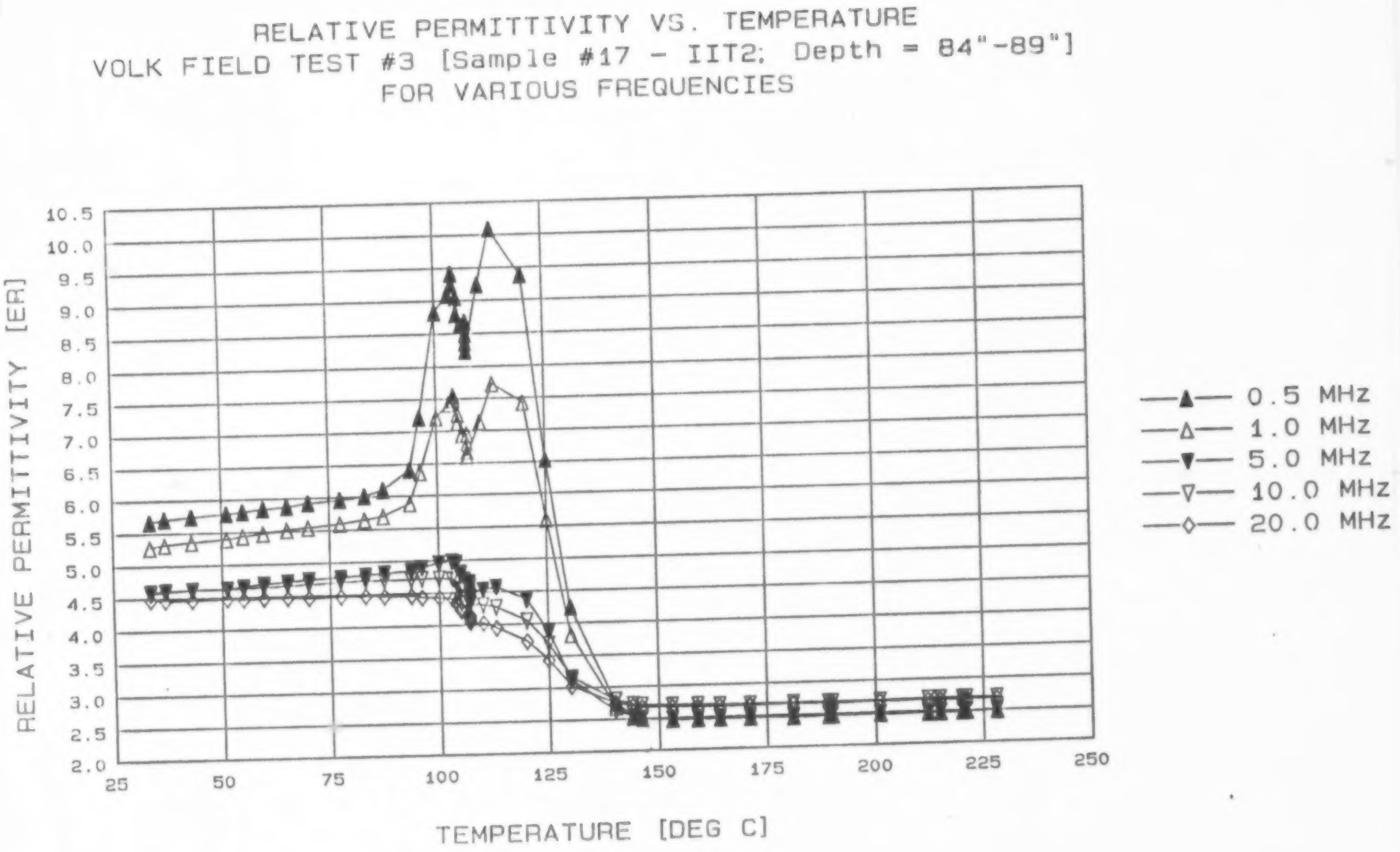

Figure 13. Relative permittivity vs. temperature for Sample #3.

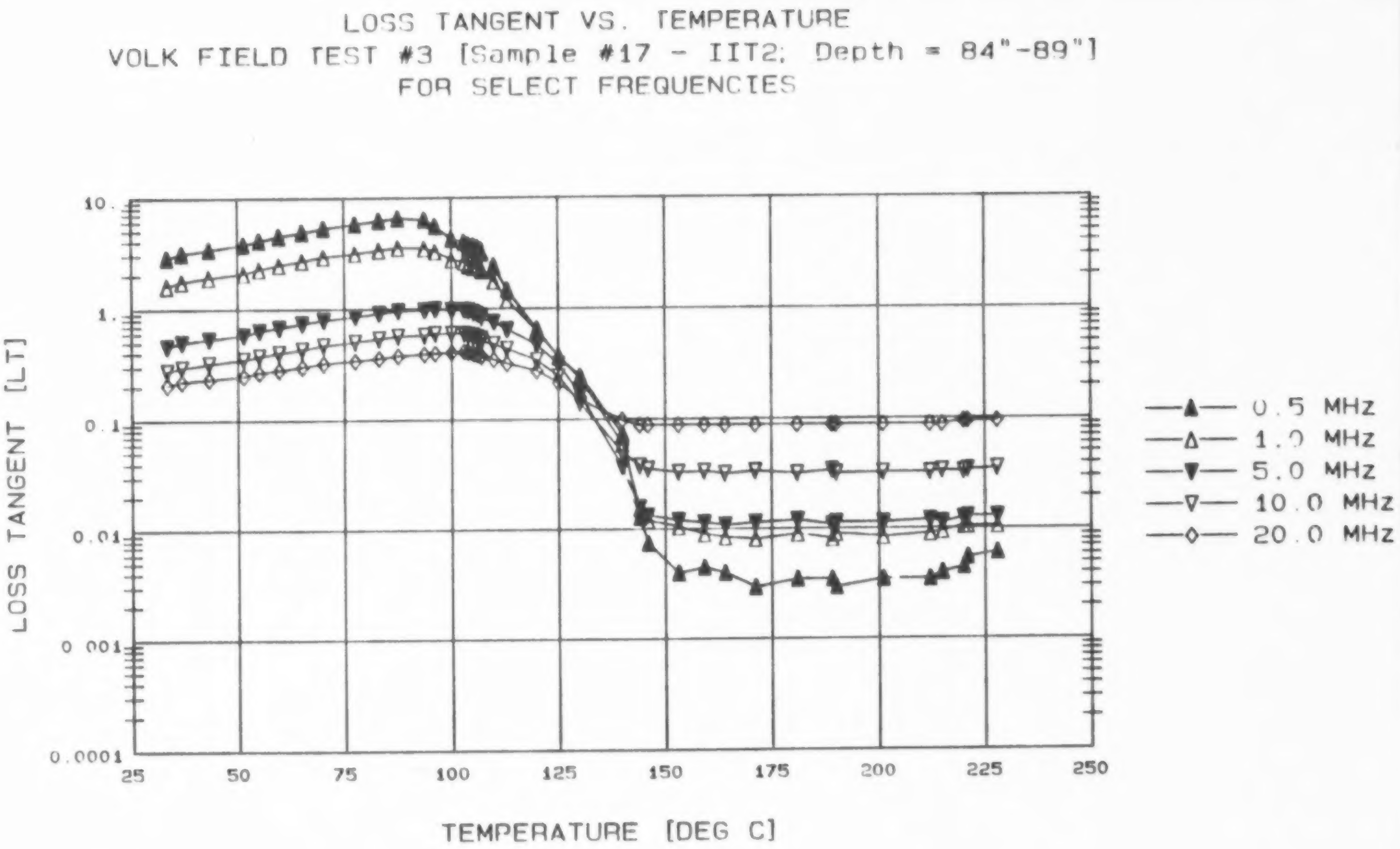

Figure 14. Loss tangent vs. temperature for Sample #3.

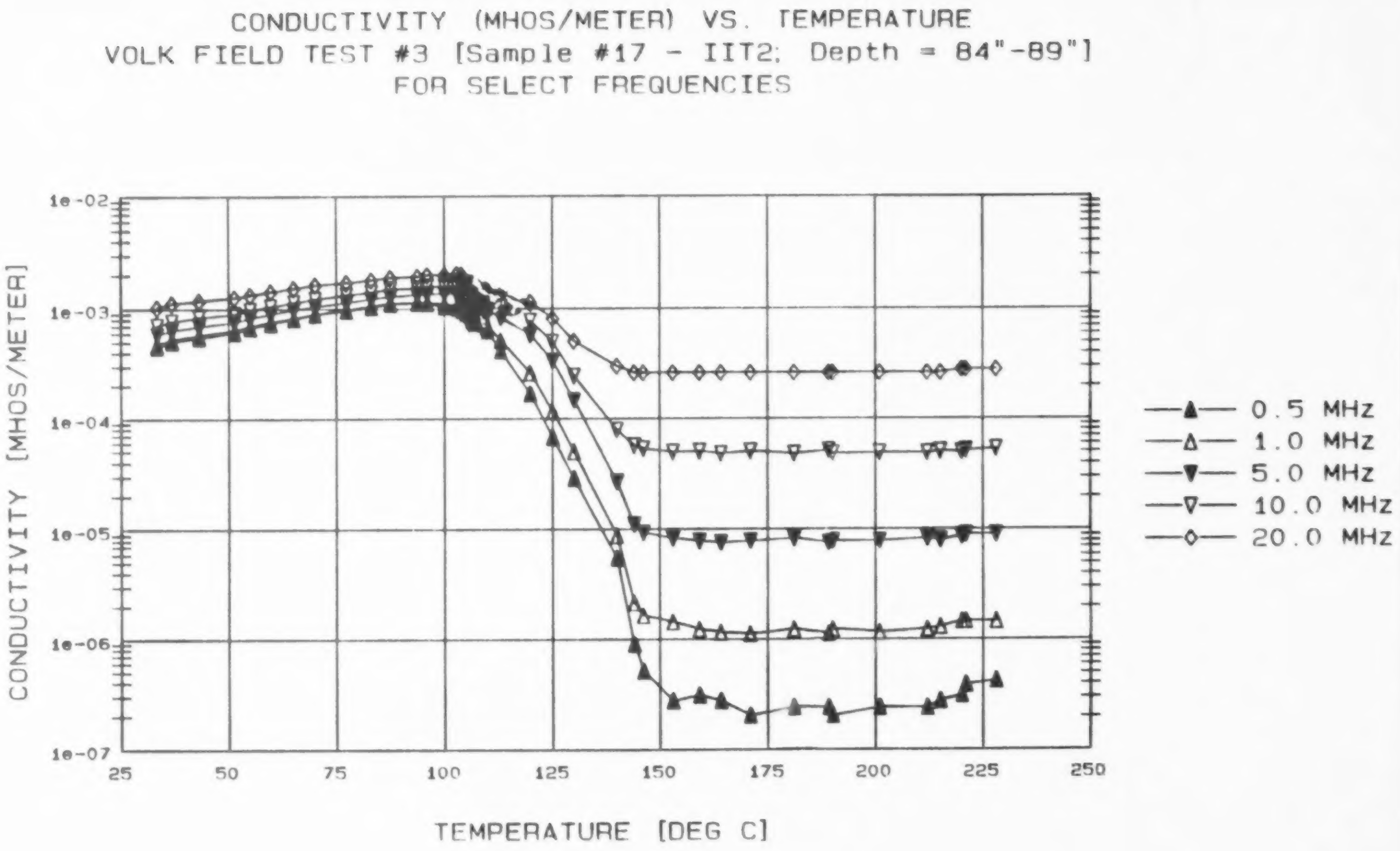

Figure 15. Conductivity vs. temperature for Sample #3.

SECTION 9

RF HEATING SYSTEM DESCRIPTION

INTRODUCTION

A fully operational in situ RF heating and decontamination system will require the design, testing, and demonstration of at least four major subsystems:

- RF energy deposition electrode array.
- RF power generation, transmission, monitoring and control systems.
- Vapor barrier and containment system.
- Gas and liquid condensate handling and treatment system.

A complete system design requires careful evaluation of various alternative designs for each subsystem and the selection of the preferred subsystems that best meet the requirements of decontamination at a particular site. Among the subsystems mentioned above, the electrode array (also called the exciter array) design is the critical item that will drive the design requirements and constraints for the other three subsystems.

Early attempts at in situ heating of earth formations utilized radiated-wave exciters which were inserted in boreholes drilled through the soils. As discussed in Reference 12, the radiated-wave exciters had poor energy efficiency due to inability to heat the soil uniformly. These exciters also radiated a significant fraction of the EM energy, especially when operating at the high power levels required to achieve economic heating rates.

Bound-wave exciter arrays avoid the problem of EM radiation by the selection of appropriate EM shielding designs. These arrays can provide uniform heating of large blocks of earth formations, minimizing hot and cold spots, thus, yielding high energy efficiency. Two types of bound-wave exciters are described below. These are:

- field-confining guide.
- fringing-field transmission line.

Considerable field experience has been gathered with the field confining guide because of its prior use for the in situ heating of Utah tar sand and oil shale deposits. The fringing field line, although not field tested, is particularly suited for heating soil to shallow depths and for the treatment of spills where the contaminant penetration is less than 24 inches. A scale model of the fringing field line was built and tested to prove its feasibility to heat soil. In the following sections the two types of bound-wave exciter arrays are described.

FIELD-CONFINING GUIDE

The triplate transmission line is an example of a field-confining guide, simply described as a coaxial cable whose conductors have been flattened from their nominal concentric circular configuration. Figure 16 illustrates the triplate line. Because of the large size of the metal plates, compared to their separation, the field between the inner conductor and the outer conductors is essentially uniform, except near the edges of the inner conductor. Soil, or any lossy dielectric placed within this electric field, would be heated in a nearly uniform manner.

Emplacement of solid metal structures underground is difficult. However, the triplate line can be adapted, using certain electromagnetic engineering techniques, to the point where emplacement is simplified. The ends of the structure are opened, making sure that the spacing between the outer plates and other geometric features satisfy certain theoretical conditions for continued, full containment of the EM energy. The solid metal sheets are then replaced by planar arrays of parallel, tubular conductors or electrodes. It can be shown that virtually all of the EM energy supplied to the structure is contained uniformly within the outer, or shield planes, if the spacing between adjacent tubular conductors is properly chosen.

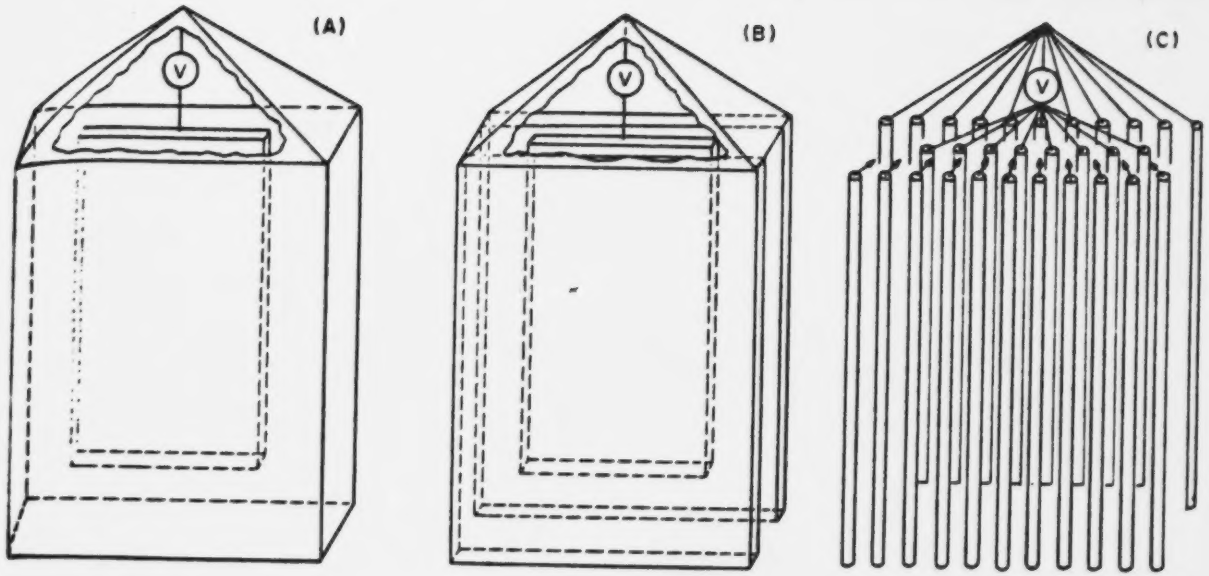

Figure 16. Triplate line conceptual design. (A) Solid wall totally enclosed cavity; (B) solid-wall cavity with side-wall removed; (C) discrete conductor realization of (B).

The triplate exciter can heat large volumes of soil to a temperature range of 150° to 400°C by creating a nearly uniform electric field in a well defined heating zone. This method is applicable for those sites where the soil contamination has exceeded a depth of 3 feet or more.

The data obtained from the dielectric parameter measurement experiments is utilized to design the electrode array and predict the variation in its input impedance as a function of the average soil temperature. Based on the data obtained to date and on past experience in heating via dielectric power absorption, final soil temperatures of 125° to 130°C can be achieved with little difficulty. Final temperatures in the 150° to 160°C range for the type of soil found at the Fire Training Pit at Volk Field appear attainable but pose some electrical difficulties. These difficulties include the need for designing dual frequency electrode array and impedance matching components.

FRINGING-FIELD TRANSMISSION LINE

Feasibility Study

A conceptual design (Reference 5) of a bound-wave fringing field line is illustrated in Figure 17. This concept makes use of the fringing fields or leakage fields that exist near a transmission line. The EM energy is first absorbed by the wet layers of soil nearest the line. As the moisture is driven out of the soil, the energy is selectively absorbed at greater depths where water is still present. The heating zone is eventually restricted because of the exponential fall-off of the fields into the soil. This line will not give a uniform heating pattern.

In practice, the fringing field line can be implemented by laying rows of horizontal electrodes on the surface of the soil which are energized with EM energy. A vapor barrier or cover will be necessary to contain the emissions from the heated soil and to permit the collection of vapors and gases for further treatment.

Although the technical capabilities and limitations of this concept are yet to be fully explored through experiments, preliminary results obtained from a working model indicate that this type of an exciter will be suitable for temperatures of 100 to 150°C and depths up to 3 feet. The schematic

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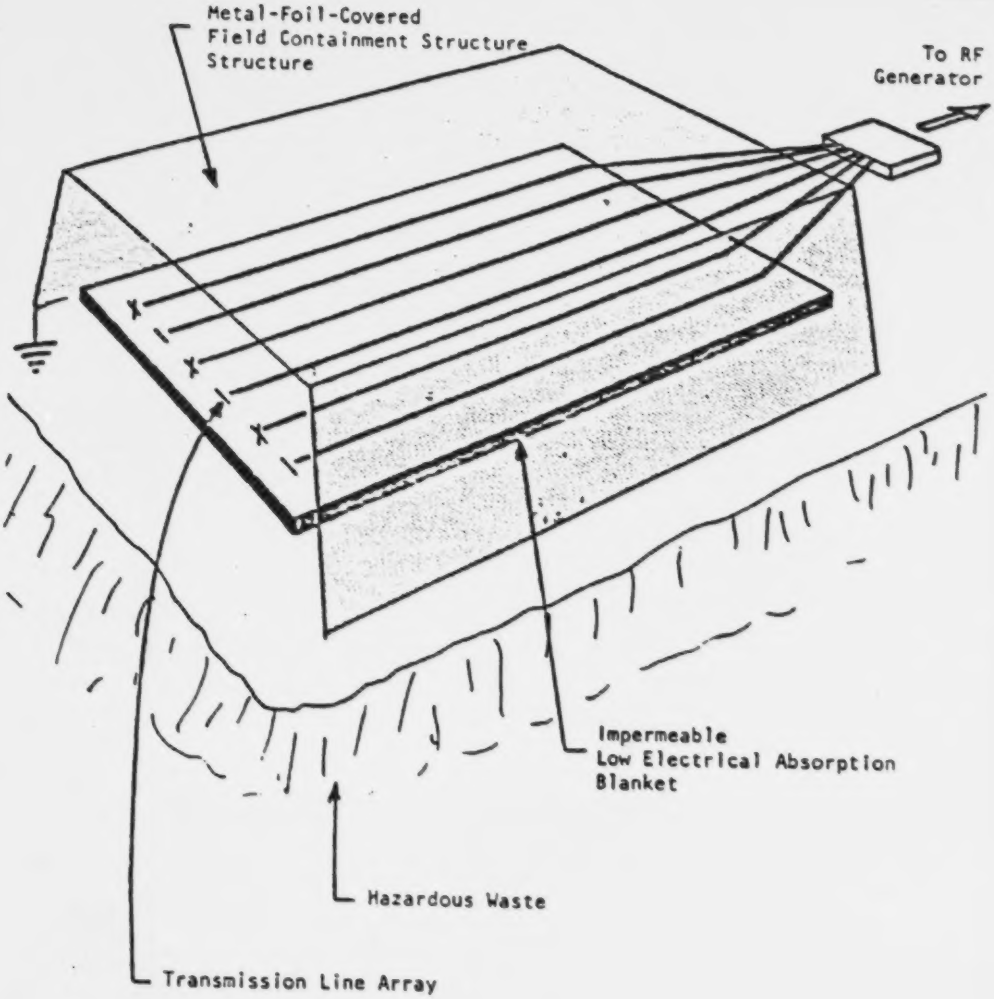
Metal-Foil-Covered
Field Containment Structure
Structure
To RF
Generator
Impermeable
Low Electrical Absorption
Blanket
Hazardous Waste
Transmission Line Array

Figure 17. A conceptual view of the fringing-field line.

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diagram of the fringing field line (Figure 17) shows rows of horizontal electrodes placed over the surface of the soil. These electrodes, when appropriately connected to an RF power source, will generate bound electromagnetic fields which penetrate downward into the soil and cause heating.

A simple module of this line, represented by a single electrode, was characterized through scale-model studies. The scale model was based on a pilot-scale line for heating of a plot of soil 10 ft x 10 ft in areal dimensions. Figure 18 illustrates a 1:3 scale model of a single electrode module of the fringing field line. The model consists of a box of dimensions 40 in x 32 in x 8 in. The box is made of brass angle-iron framework to which brass sheets are attached with screws. The brass sheet is used for all faces which have the 8-in dimension. The two longer walls with dimensions of 32 x 40 in are made of stretched brass wire mesh backed on the outside with heavy fiber glass sheet insulation. A horizontal electrode made from 2-in diameter thin-wall copper tubing is shown to run through the center of the box. Soil was packed to a depth of 14 inches below the electrode.

The RF power is supplied to the electrode by means of a coaxial cable in which the center conductor is connected to the electrode and the outer, or guard conductor, is attached to the brass box. Thermowells were inserted at various locations inside the soil bed to measure the temperature distribution during heating. Figure 19 illustrates the location of each of the thermowells used in the first test of the model and Figure 20 illustrates the location of the thermowells for the second test.

Soil Heating Test 1

In test 1, top soil obtained from a nursery was packed into the box. The moisture content of the soil was adjusted to approximately 10 wt%. The soil weight was 158 lbs, equivalent to an average bulk density of 61 lbs/cu ft. It was observed that the soil contained a large fraction of humus, loam, and other vegetable matter. No attempt was made to determine the percentage of organic matter in the soil.

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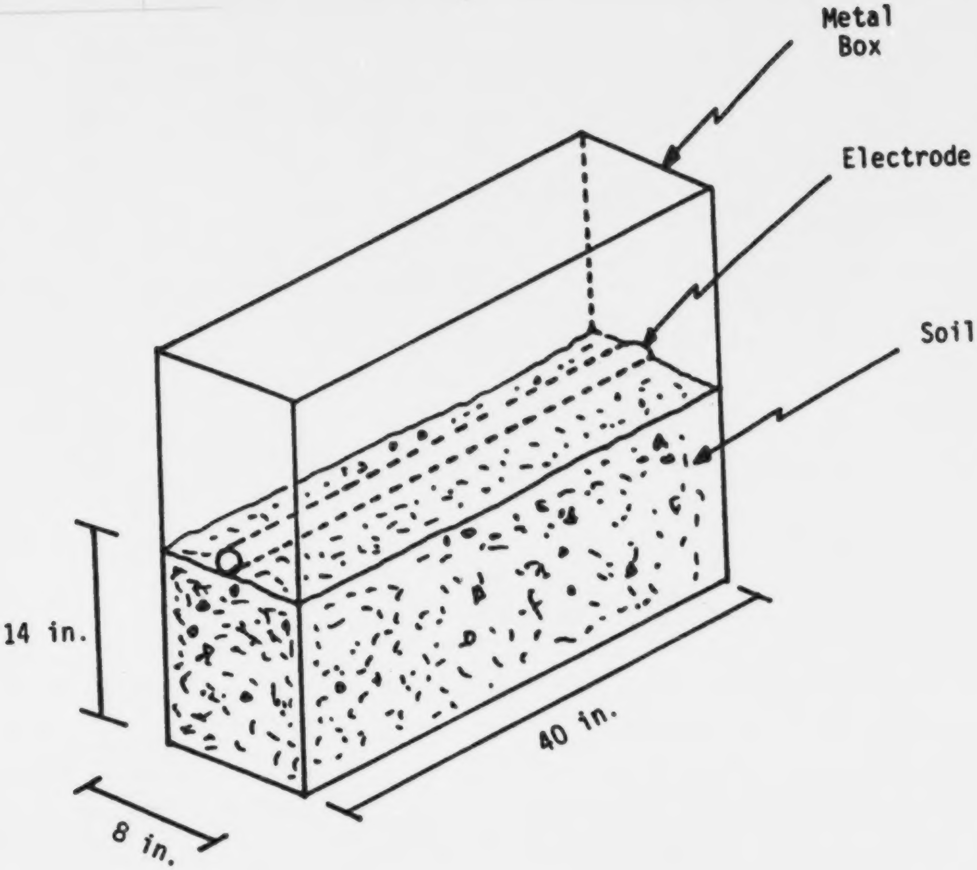

Figure 18. Scale model of a single-electrode module of the fringing field line (based on 10 x 10 ft field demonstration scale).

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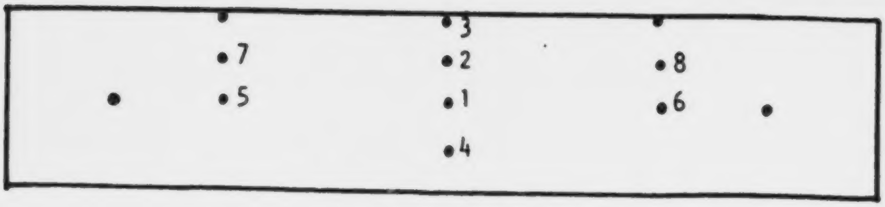

Top View

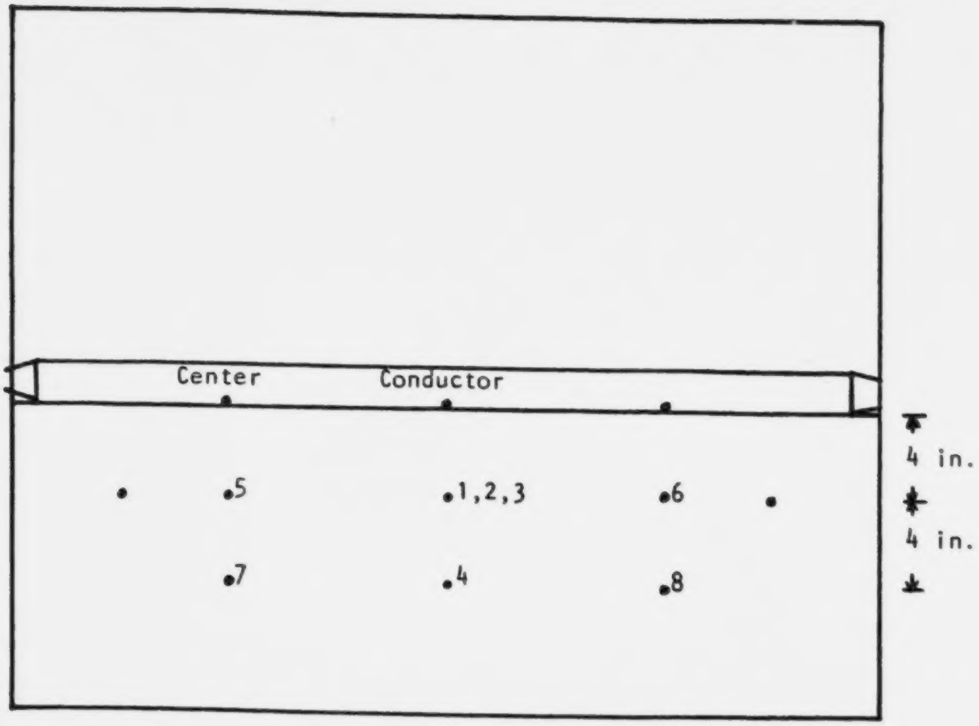
Center
Conductor
4 in.
5
1,2,3
6
4 in.
7
4
8

Figure 19. Thermowell location for Test 1 of the model.

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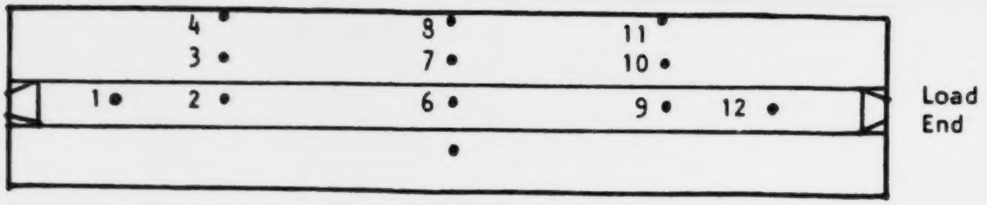
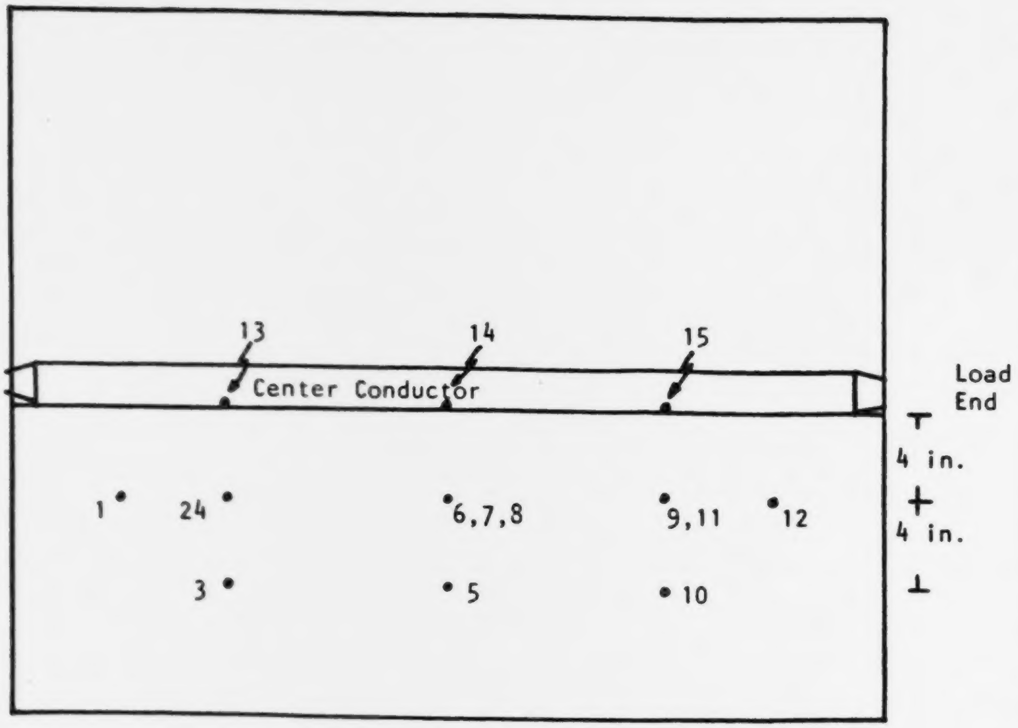

4
3
1
2
8
7
6
11
10
9
12
Load
End

Top View


13
14
15
Center Conductor
Load
End
4 in.
4 in.
1
24
6,7,8
9,11
12
3
5
10

Side View

Figure 20. Thermowell location for Test 2 of the model.

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The packed soil was heated by the application of RF energy using a 1 kW power source. Figure 21 illustrates the average temperature rise of the soil as a function of time. The temperatures inside the electrode wall in contact with the soil, and at depths of 4 and 8 inches below the electrode are plotted. It was observed that the average temperature of the soil at a depth of 4 inches rose at a uniform rate of 19.5°C/hr, in the temperature range of 24 to 200°C. The test was terminated at that time (after 9.1 hours) due to failure of a solder joint used to connect the electrode to the RF coaxial cable. However, the soil temperature continued to rise even though the RF power input was zero. It was observed that the upper surface of the soil was glowing red-hot indicating auto-ignition of the organic matter.

The average temperature at a depth of 8 inches was 75°C when the test was terminated at the end of 9.1 hours. A depth range of 4 to 8 inches in the scale model represents a depth of 12 to 24 inches in the field-scale. At the end of the test, the average temperature gradient in the vertical direction was 31.2°C/in. Based on this, the temperature at a depth of 6 inches was estimated to be 137°C.

Soil Heating Test 2

In the second test of the fringing field line, a sandy soil was obtained. This was done to avoid the problem of auto-ignition of the organic matter encountered during the first test. In addition, KPEG, preheated to 80°C, was added after the soil, at a depth of 4 inches, had achieved a temperature of 112°C. The purpose of this test was to determine whether heating could be resumed after the addition of KPEG.

In this test, twelve thermowells were used to measure the temperature distribution in the soil. In Figure 22 the average temperature inside the electrode and at a depth of 4 and 8 inches below the electrode is plotted. The average heating rate was 3.4°C/hr. This lower heating rate was realized due to two reasons. The average input RF power was 342 watts as compared to 497 watts supplied in the first test. The second reason for the lower heating rate resulted from four hours of down time due to problems with the matching network requiring repairs. The average heating rate at the 8 in. depth was 2.42°C/hr as opposed to 5.6°C/hr in the first test.

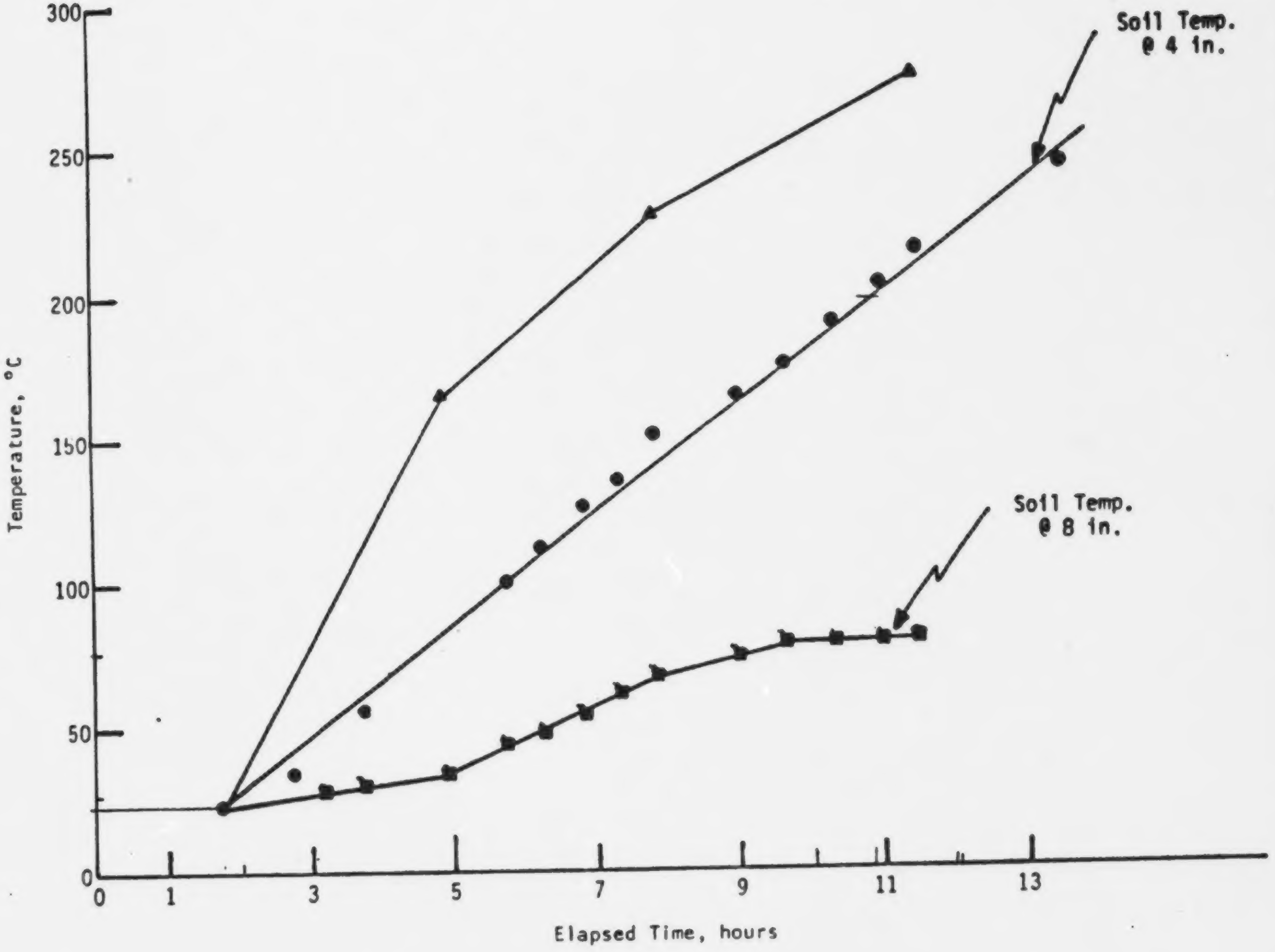

Figure 21. Soil temperature profile during scale-model tests of the fringing field line (Test 1).

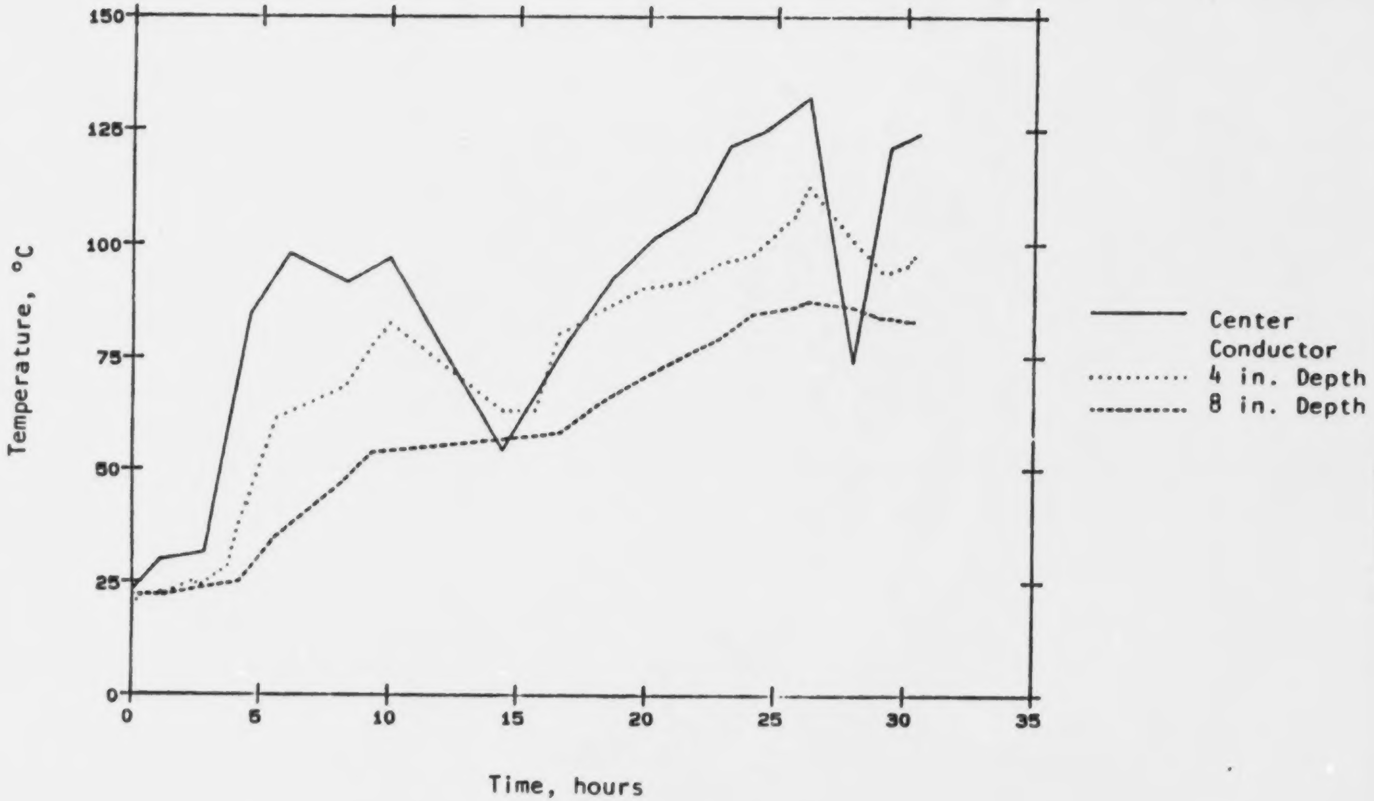

Figure 22. Fringing field line scale model heat Test 2 temperature ramp.

In the second test an average temperature of 87°C was achieved at a depth of 8 in. after 26 hours of operation. At the end of 26 hours, when the temperatures at the 4 and 8 in. level were 112° and 87°C respectively, the power was switched off and KPEG was added to the system. Approximately 27.5 lbs of 90% KPEG, 10% H_2O solution were added to the soil by pouring the preheated KPEG over the top surface of the soil. The KPEG addition took approximately 35 minutes at the end of which time no free-standing KPEG was visible on the soil surface. Heating was resumed for 2.25 hours to verify the ability to resume power delivery to the load (Figure 22).

The results of these experiments show that the fringing-field line can be used to heat soils to depths of 12 to 24 inches. However, additional effort is necessary to develop scale-up and design data. It was also shown that it is easy to auto-ignite soils containing plant and vegetable organic matter provided good aeration is provided. Additional work is necessary to evaluate the effect of auto-ignition to help soil decontamination through combustion of the hydrocarbon contaminants along with the organic matter.

The fringing field line can be readily used for the thermal treatment of soil spills which contain solvents such as tetrachloroethylene, chlorobenzene, etc. Data presented in sections 3 and 4 demonstrate the feasibility of removing these and other similar contaminants in the 90 to 130°C temperature range.

SECTION 10

COST OF RF IN SITU TREATMENT

A cost estimate was previously[12] made for the treatment of soil by in situ radio frequency heating. This estimate was developed for a site containing solvents and jet fuels having a typical boiling range of 80 - 230°C. A conceptual design of an RF treatment system was made to develop estimates of major capital equipment costs and operating costs of the system. The design is based on the triplate exciter electrode array for treatment to a depth of 8 ft. The results of the cost study are summarized below.

CONCEPTUAL DESIGN

The design is based on heating 96 ft x 96 ft modules of contaminated plot. Thus, if a contaminated site is larger than the module size, then the entire site will be treated by operating several modules. The module will be subdivided into blocks. Figure 23 illustrates the plan view of a module which has been subdivided into 9 blocks, each of dimensions 32 ft x 32 ft. The plan view of the electrode array arrangement in each block is shown in Figure 24.

Prior to installation of the electrodes the site may require leveling with a grader. The hole locations will be staked and the holes drilled. Various methods are available for drilling the holes but it is expected that conventional well drilling equipment will be used. For soft sandy soil, a hand or motor-driven auger can also be used. Many new short depth borehole forming tools are being developed by the gas industry. These include air jet ("air-knife") and water-jet assisted devices. In most soils, the 8-ft holes can be formed in less than one minute with a water-jet system. The diameter of the holes will be 4 to 4.5 inches depending upon the OD of the electrodes. It is expected that the electrode diameter will be 3.5 to 4 inches. The electrodes will be dropped into the boreholes. No grouting was considered in this design.

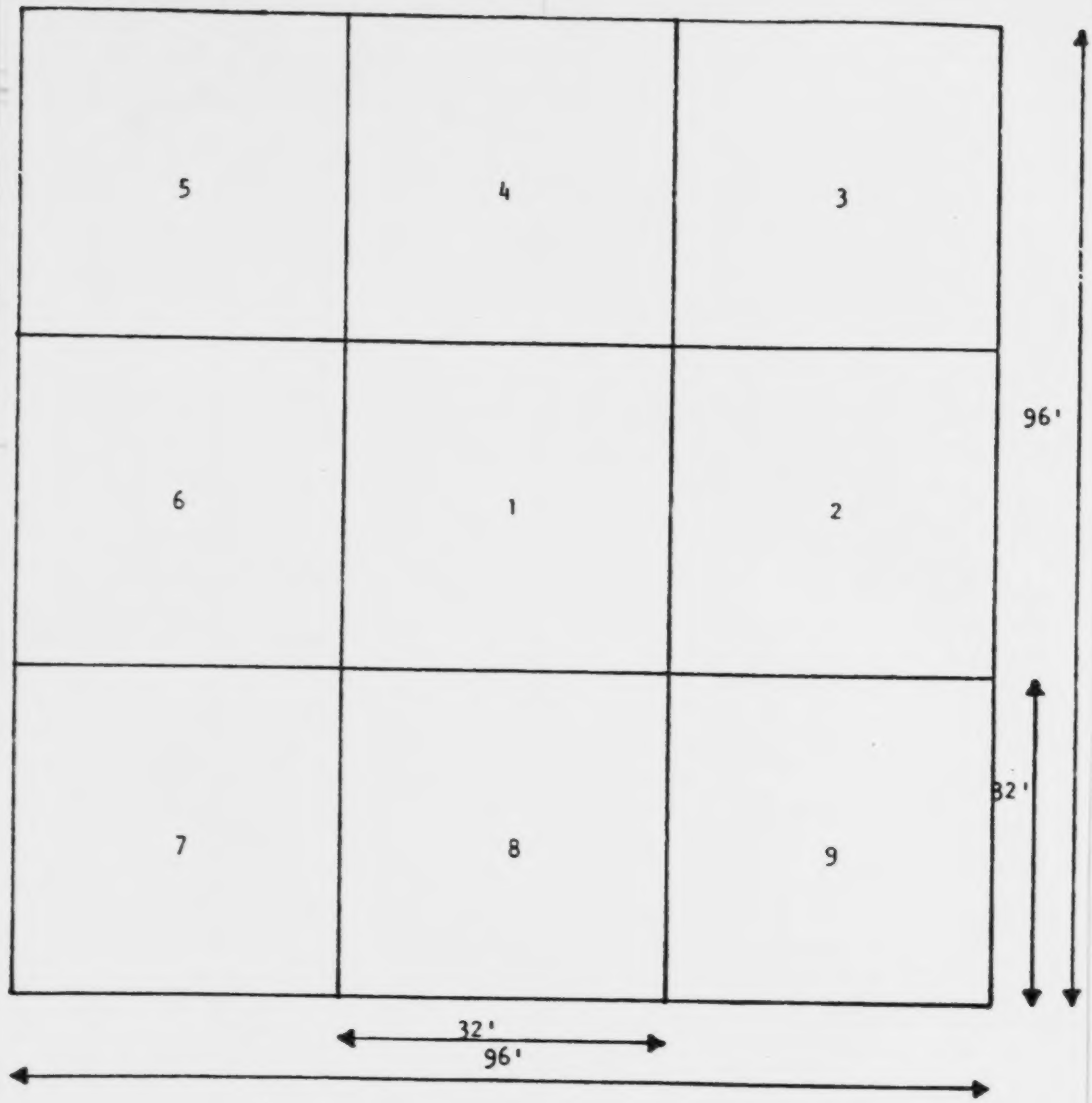
5
4
3
96'
6
1
2
32'
7
8
9
32'
96'

Figure 23. Plan view of a "module" or plot of soil subdivided into nine heated blocks.

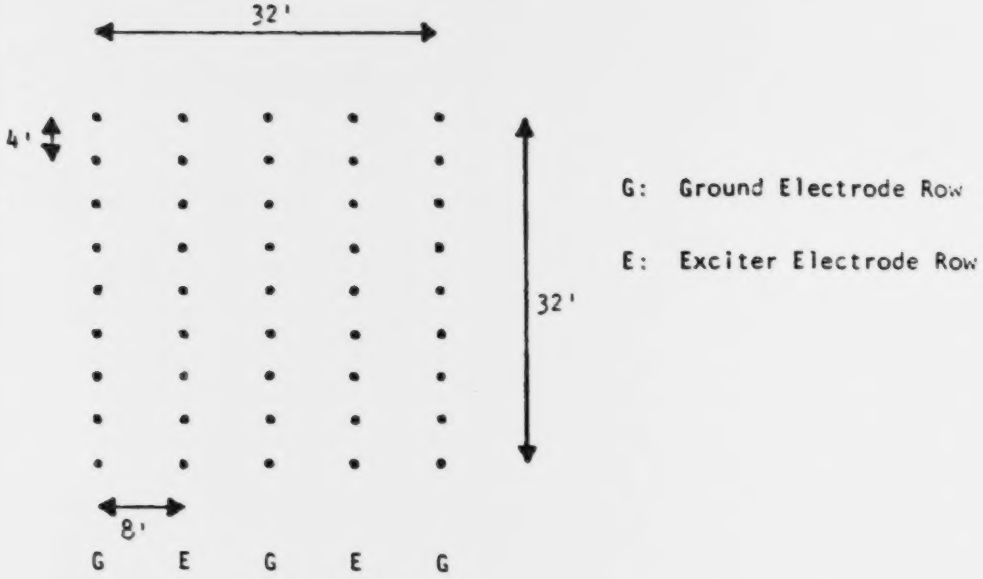
32'
4'
32'
G: Ground Electrode Row
E: Exciter Electrode Row
8'
G E G E G

Figure 24. Block electrode arrangement.

All the electrodes within each row will be electrically connected with metal straps. The exciter electrodes will be attached to the center conductor of the coaxial transmission line supplying power from the RF transmitter, via an interconnecting transition section and matching network. The ground electrodes will be connected to the outer conductor of this transition section. The function of the matching network is to provide for efficient transfer of RF energy from the transmitter to the triplate line.

Vapor Barrier and Collection System

A vapor barrier will be necessary to contain and collect the gases and vapors rising to the soil surface. Conceptual designs of two such barriers were prepared earlier and are described in Reference 5. In Figure 25, an alternative design of a vapor barrier is shown for a triplate line embedded in soil. This design is based on commercially available prefabricated A-frame buildings. The siding will be replaced with a disposable sheath made from metal foil which is protected by a coating to prevent corrosion. Engineering design of these barriers has not been developed as it was beyond the scope of this effort.

The vapors will be removed from the vapor barrier zone by an induced draft fan which will keep the entire enclosed zone under a vacuum of the order of 1 to 10 mm of H_2O. This will ensure that the vapors do not escape from the barrier in the event of a leak. The collected gases and vapors will have to be treated on-site. Figure 26 is a block diagram of a vapor and gas treatment flow sheet which was used to estimate the cost of gas and vapor treatment. The essential steps of the flow sheet are: gas cooling and vapor condensation, gas/liquid separation, and a carbon-bed treatment. The liquid stream will be treated on-site by separation of aqueous phase from organic phase(s); neutralization, filtration and carbon treated of the aqueous phase. The organic phase will be sent for ultimate disposal in an approved incineration facility.

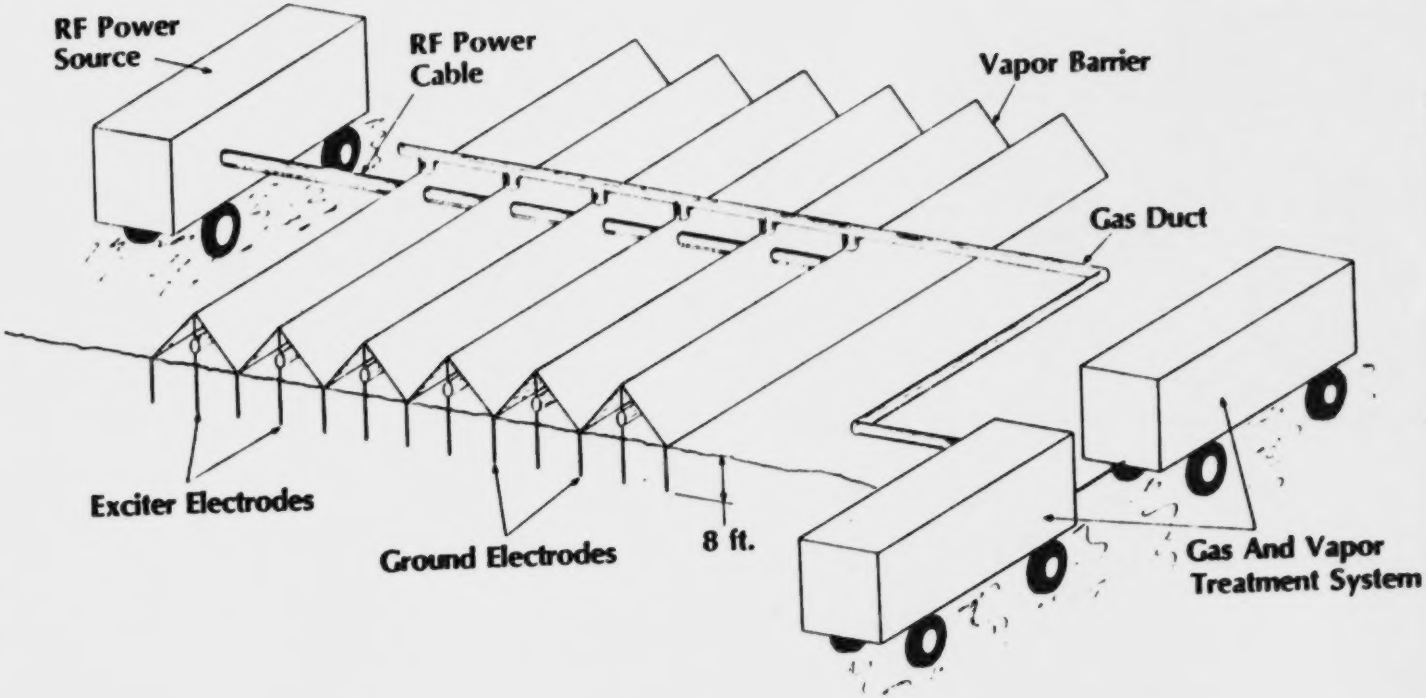
RF Power Source
RF Power Cable
Vapor Barrier
Gas Duct
Exciter Electrodes
Ground Electrodes
8 ft.
Gas And Vapor Treatment System

Figure 25. Conceptual design for a vapor barrier and triplate line.

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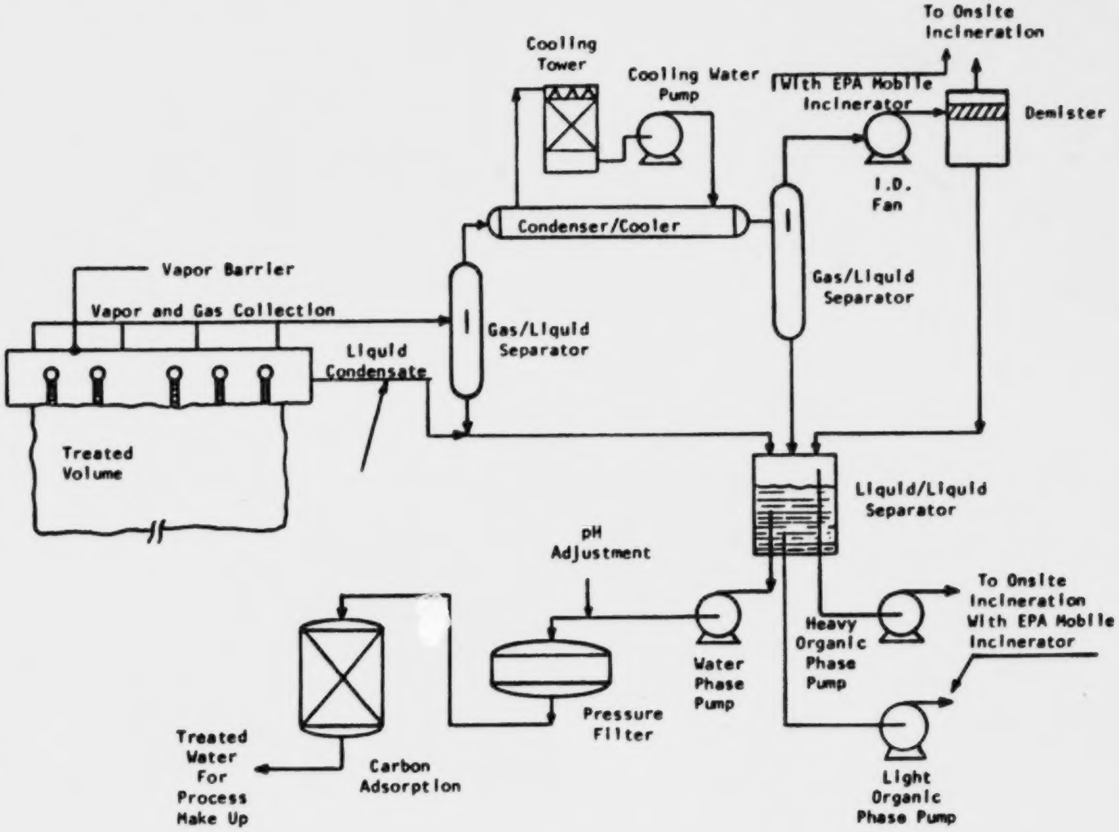
To Onsite Incineration
With EPA Mobile Incinerator
Cooling Tower
Cooling Water Pump
Demister
I.D. Fan
Condenser/Cooler
Gas/Liquid Separator
Vapor Barrier
Vapor and Gas Collection
Gas/Liquid Separator
Liquid Condensate
Treated Volume
Liquid/Liquid Separator
pH Adjustment
To Onsite Incineration With EPA Mobile Incinerator
Heavy Organic Phase Pump
Water Phase Pump
Pressure Filter
Treated Water For Process Make Up
Carbon Adsorption
Light Organic Phase Pump

Figure 26. Vapor treatment system flow diagram.

PROCEDURE FOR ESTIMATING COST

The cost of heating a plot or module of contaminated soil to a temperature range of 100° to 250°C was calculated by separately estimating the capital and operating costs. The estimate was developed for a module 96 feet by 96 feet by 8 feet. The moisture content in the soil was assumed to vary in the range of 5 to 20 weight percent.

A treatment temperature range of 100° to 250°C was selected based on the boiling range of the contaminants expected in the soil at various Air Force bases. As mentioned in Section 2, the normal boiling range of the known contaminants is 80° to 232°C. It has been shown by the feasibility study that up to 95 percent removal of tetrachloroethylene can be achieved at temperatures 20° to 30°C lower than its normal boiling point. For soils containing jet fuel, the feasibility study has shown that 90 to 99% removal can be achieved at a treatment temperature of 150°-160°C. The base-case cost estimate was developed for a treatment temperature of 170°C for soil containing an average of 12 percent water.

The cost estimate was developed by separately estimating the cost of capital equipment and the operating costs. The capital cost was developed for a treatment system using a 1.0 MW RF power source.

The capital cost was amortized on a per module basis by estimating the number of modules treated per year. A finance charge of 20 percent per year was assumed over the 20-year life of the capital equipment.

The operating cost was developed by separately estimating two cost elements: the fixed operating cost and the variable operating cost. Fixed operating costs consist of those costs that are independent of the treatment duration. The costs of site preparation, installation and checkout of the system, application for permits and licenses, etc., are examples of fixed operating cost.

Variable operating costs depend on duration of treatment, e.g., AC power cost, operating labor cost, consumable supplies, fuel, etc.

In the following subsections a summary of the assumptions and the cost estimate is presented.

Assumptions

The cost estimate was developed for a module of dimensions 96 feet by 96 feet. It was assumed that at a typical contaminated site several such modules would be operated for the cleanup of the entire site. Cost elements were identified that are common for the treatment of a site. Examples of such cost elements are; road improvement, temporary AC power supply, transportation of the treatment system to the site, licenses, permits, etc. The cost of these activities was recovered by assigning a prorated share on a per-module basis.

The following additional assumptions were made in the cost estimate:

- Cost was developed for a system using a fully tested and a mature technology.
- Average labor rate for engineering personnel is $20/h, for supervisory personnel $28/h, and for operators $15/h. In addition, a 20 percent allowance for fringe benefits has been added.
- The RF power source has an AC to RF conversion efficiency of 85 percent.
- RF transmission and distribution efficiency is 95 percent.
- RF power source operates for 23 h/day.
- RF power source is operated at 100 percent of its rated capacity.
- No soaking time is required after achieving the final temperature.
- Average annual capital charge for the capital equipment is 20 percent.
- Capital equipment will be amortized over a life of 20 years and over the number of modules treated per year.
- Treatment site is located within 0.5 mile of an AC power source.
- A temporary AC power line will be required to supply up to 1.2 MW at the site.
- Purchased AC power costs $0.055 per kWHr.

COST ESTIMATE

An estimate for the capital cost of a treatment system based on a 1.0 MW RF power source is given in Table 19. As shown, all the sub-systems

TABLE 19. SUMMARY OF CAPITAL COST FOR A 1.0 MW SYSTEM

	Subsystem Description	Quantity	Total Cost
1.	1.0 MW RF power source, dummy load, RF power transmission, and control system	1	1,000,000
2.	Vapor barrier and gas collection system	2	96,000
3.	Gas, vapor, and condensate treatment system	2	300,000
4.	Analytical instrumentation and safety equipment	2	100,000
5.	Tools	1	10,000
6.	Backhoe	1	40,000
7.	Utility vehicles (pickup, etc)	2	40,000
8.	Electrode system for 2 modules at 2650 ft/module	2	10,600
TOTAL CAPITAL COST			$ 1,596,600

associated with vapor containment, collection, and treatment are duplicated. The reason for doing this is to maximize the utilization of the two capital-intensive subsystems: the RF power source and the transmission system. It was calculated that the heating and treatment time for a module varies from 13 to 37 days. However, the equipment setup and tear-down time is approximately 21 days. The RF power source can be more effectively utilized if all the other systems are duplicated so that the power source idle time between two modules can be minimized.

A conceptual design of a gas, vapor, and condensate treatment system was developed earlier (Reference 5) for a 20-MW RF heating system. The capital cost of a similar, scaled-down version of the treatment system is shown in Table 19. It is estimated that in the base case, approximately 127,000 gallons of condensate containing 99.9 percent water will require treatment. The treatment will consist of separation of aqueous from nonaqueous phases, followed by pH adjustment, filtration, and carbon-bed adsorption of the aqueous phase. The treated water will be recycled and used to meet process-water requirements. However, it is assumed that at the end of the soil treatment, the treated water will be sprayed back on the hot soil surface to speed cooling of the module.

The hot gases will be treated onsite by cooling, condensing the vapors, condensate separation from gas, gas demisting, and carbon adsorption. As mentioned earlier, the vapor barrier is made from the structural components of commercially available A-frame metal building, equipped with specially designed disposable metal foil sheath for siding. The costs shown in Table 19 were derived from the cost of commercially available A-frame buildings.

The capital equipment costs will be amortized over the total number of sites treated during the life of the capital equipmient. The treatment time for a module varies between 13 days to 37 days. For the purpose of estimating the number of modules that can be treated per year, the treatment duration for the base case of 170°C, 12 percent moisture will be used. The base case heat-up and treatment time is 24 days. Thus, the average treatment will be performed in approximately 45 days after allowing for set-up and tear-down. Using a single stream, approximately 8 modules can be treated per year or 160 modules over the life of the equipment. If the double stream option is implemented, the number of modules treated per year increases to 14. The annual capital cost of the equipment, therefore, will be amortized over the number of modules treated per year, for the double stream option.

The depreciation for capital equipment will be calculated based on a uniform straight-line depreciation over 20 years, at an average capital charge of 20 percent per year. The yearly amortization charge of the capital cost was obtained from annuity tables. Based on these tables, $327,880 per year are required to meet the charges on capital cost. To find the cost per module, this amount was charged to 14 modules per year. The fixed capital cost then becomes $23,420 per treated module.

Total Treatment Cost

In Table 20, the treatment cost of a contaminated module 96 feet by 96 feet by 8 feet is given as a function of moisture content and temperature.

The cost for the treatment of a contaminated modules varies between $130,000 and $254,000. The cost for treatment of the base case is $188,000. A 20 percent contingency allowance has been added.

TABLE 20. TREATMENT COST PER MODULE

Moisture Content %	Thousands of Dollars				
	Temperature, °C				
	100	125	150	170	250
5	130	136	141	147	167
10	158	166	172	177	197
12	172	177	183	188	208
20	219	224	229	234	254

In Table 21 the treatment cost per 100 pounds of soil is given as a function of temperature and moisture content. The cost per 100 pounds of soil varies between $1.47 to $2.87.

TABLE 21. TREATMENT COST FOR 100 POUNDS OF SOIL

Moisture Content %	Treatment Cost, $/100 lbs				
	Temperature, °C				
	100	125	150	170	250
5	1.47	1.54	1.59	1.66	1.89
10	1.79	1.88	1.94	2.00	2.23
12	1.94	2.00	2.07	2.12	2.35
20	2.47	2.53	2.59	2.64	2.87

The soil sample on which experiments were performed during this project was obtained from Tyndall AFB and Volk ANGB. These samples had an average moisture content ranging between 3 to 4 percent. For this type of soil containing tetrachloroethylene, a maximum treatment temperature of 125°C should be sufficient to remove 95 percent of the contaminant. For this case, treatment cost can be estimated from Table 21 by extrapolating the cost figures given under the column for 125°C. Based on such an extrapolation the treatment cost is projected as $1.41 to $1.48 per 100 pounds of soil.

SECTION 11

PILOT-SCALE FIELD TEST PLAN

INTRODUCTION

Two alternative pilot-scale test designs were considered before a final selection. The first pilot-scale test design was based on heating the soil packed in a large reactor. It was proposed to pack the reactor with 5000 lbs of soil pre-spiked with the contaminants of interest. The main advantage of such a design is that it can be performed in a pilot plant as opposed to the field, thus providing substantial cost savings associated with mobilization, site preparation, installation of AC power at the site, etc. The second alternative considered was to conduct an in-situ test at Volk Field ANGB, Camp Douglas, Wisconsin. In this test, approximately 500 cu ft of soil, weighing 70,000 lbs would be heated.

The first alternative mentioned above was rejected in favor of the in-situ field test. The main reason for a rejection of the first design was serious concern about the feasibility of spiking 5000 lbs of soil uniformly to the desired concentration level. Previous laboratory attempts at the preparation of 11 lb of spiked soil containing 10-50 ppm of chlorobenzene and tetrachloroethylene were unsuccessful. The problems are related to the high volatility of the contaminants and the numerous material handling steps necessary for spiking and homogenizing the soil. During these steps, significant loss of the contaminants occurred. Moreover, in the reactor pilot test, the spiked soil would have to be packed in the reactor approximately five weeks before commencement of heating. This time was necessary to insert the electrode array, sample the soil, install the vapor barrier, and the vapor collection and treatment system. During these 5 weeks, additional loss of spikes was anticipated due to volatilization.

The above concerns were discussed with the project monitor and a decision was taken to perform the pilot test in the field. It was further decided that the field test designs would be conducted under the auspices of this grant but the field test would be funded by the USAF under a separate program to be proposed by IITRI.

In the following sections, the field test design is described.

FIELD TEST OBJECTIVES

The major objective of the proposed field test program is to perform an in situ radio frequency heating and soil decontamination test to prove the feasibility of the process under field conditions. Another objective of the test is to assess the migration, if any, of the contaminants from or into the heated zone from the surrounding cooler zones.

The proposed field test will be conducted at a fire training pit located at Volk Field ANGB, Camp Douglas, Wisconsin. The site has a wide range of contaminants representing various jet fuel fractions, solvents, degreasing agents, etc. The boiling point range of the compounds is 60° to 300°C. It is planned to heat 60 to 80 ft^2 of the surface area to a depth of 6 to 9 ft. The total heating, decontamination, and cool down period will span a period of 4 weeks. The test will utilize an IITRI owned 40-kW, mobile HF band radio transmitter.

TEST DESCRIPTION

Triplate Electrode Array Design

It is planned to heat a 6 ft x 12 ft area of the fire training pit using three rows of vertical electrodes emplaced in bore holes drilled through the soil. Figures 27 and 28 illustrate the design of the electrode array and the vapor barrier. The dimensions of the test volume and power level requirements are summarized in Table 22.

In each of the three electrode rows, there will be 13 electrodes. The electrodes will be made of 3-in. diameter copper tubing. A 12-in. wide trench is shown outside the electrode array. It is planned to line the outer walls of the trench with transite sheet to mitigate lateral migration of fluids

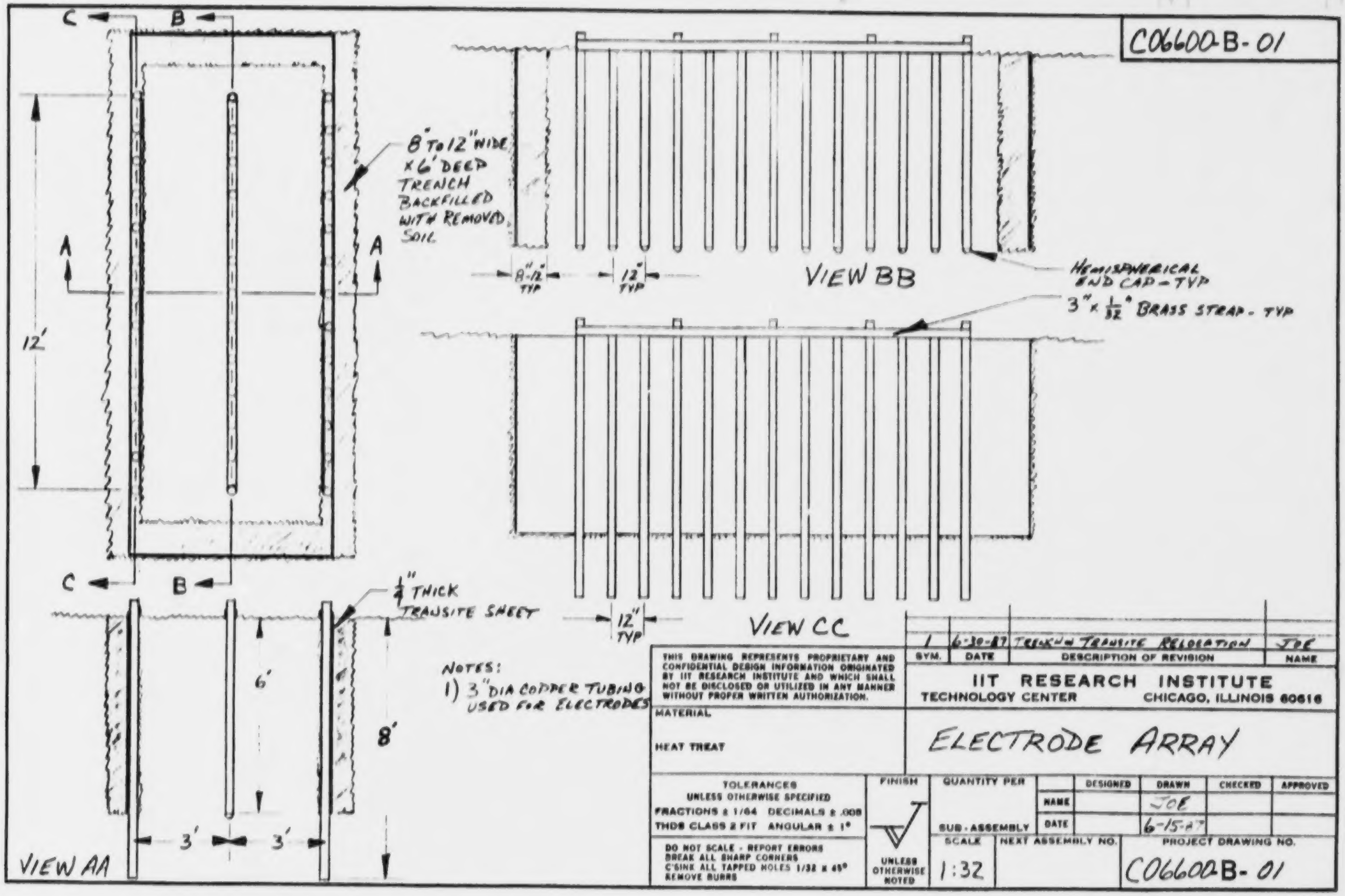
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Figure 27. Electrode array design for Volk Field test.

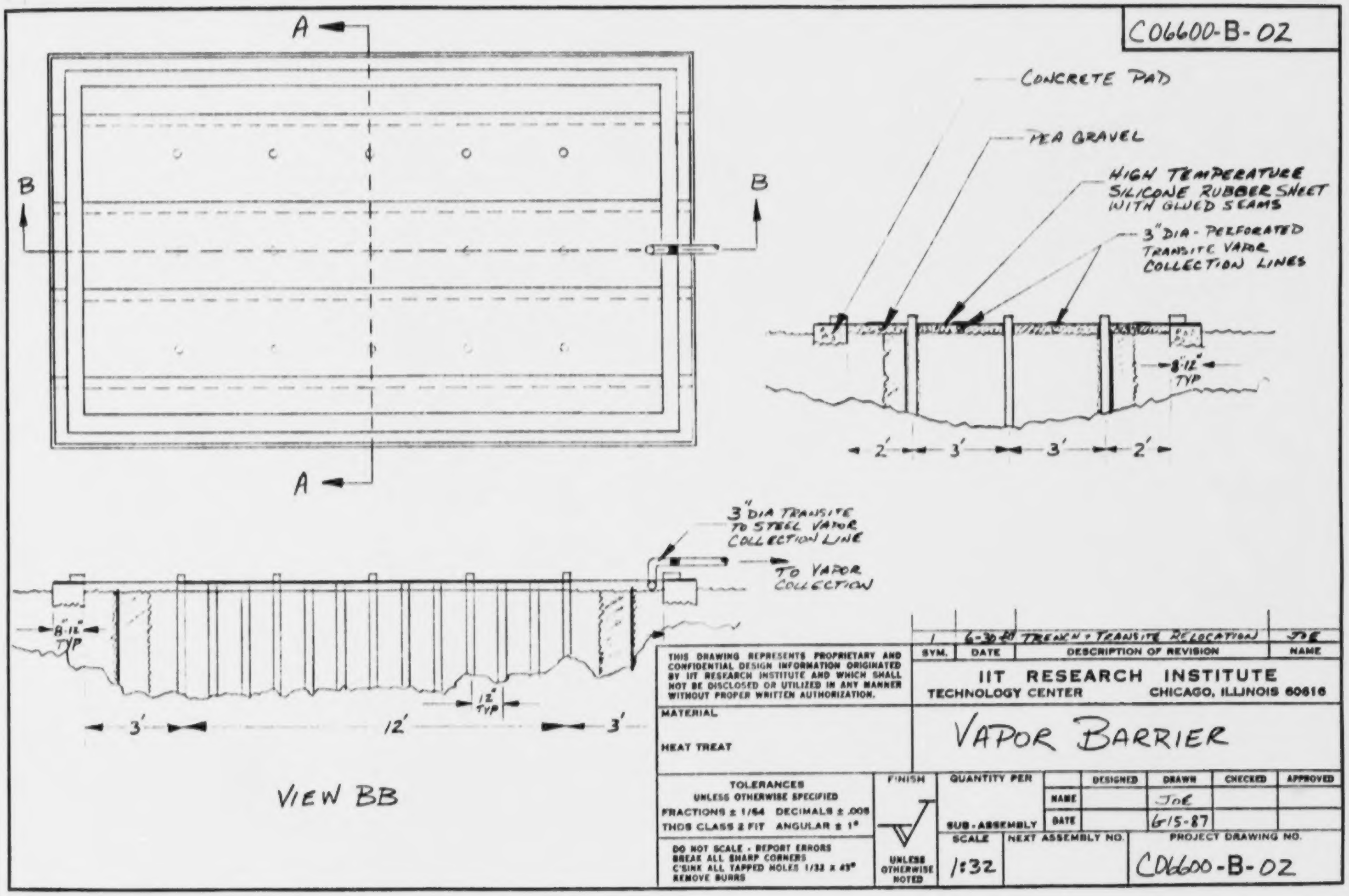
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Figure 28. Vapor barrier design for Volk Field test.

TABLE 22. DESCRIPTION OF FIELD TEST

Dimensions: Area 6 ft x 12 ft	72 ft^2
Ground Electrode Depth	8 ft
Exciter Electrode Depth	6 ft
Volume Heated, 6 ft x 12 ft x 7 ft	504 cu ft
Mass Heated, (ρ = 2.2)	69,000 lbs
Water in Place @ 5% by Weight	3,450 lbs
Hydrocarbons in Place @ 1,600 ppm*	110 lbs
Chlorinated Hydrocarbons in Place at 3 ppm*	0.21 lbs
Average Water Boil-Up Rate	1.4 gph
Average Rate of Power Delivery:	
Below 100°C	30 kW
At 100°C	30 kW
Above 100°C (After Water Boil Off)	10 kW
Time to Reach 100°C	2.5 days
Time at 100°C	4 days
Time to Reach 150°C from 100°C	2.5 days
Time at 150°C	4 days

*Based on analysis performed by SAI, Inc.

through the heated volume. After placing the liner, the trench will be backfilled with clean soil of a similar texture obtained from the Base.

The vapor barrier, shown in Figure 28, will be made from a 0.125-in. thick silicon rubber sheet. This sheet will be bonded to a concrete pad poured around the outer edges of the trench. The concrete pad will form a "picture frame" around the entire heated zone. The silicon rubber sheet will stretch from end-to-end of the pad and will be bonded to a metal plate imbedded in the pad.

Below the vapor barrier, two perforated gas collection pipes will be laid horizontally over the surface of the soil. Outside the heated zone, these lines will be manifolded together and connected to the vapor collection system.

There will be 30 thermocouples attached to the inner wall of the electrodes. In addition, there will be 18 thermowells imbedded in soil for measurement of temperature by insertion of a thermocouple whenever RF power is switched off. It is anticipated that the RF power will be switched off once every 6 to 10 hrs for making these and other electrical measurements.

RF Transition Section

The RF transition section is a carefully designed geometric structure which is utilized to change the shape of the coaxial RF power cable into a triplanar RF cable which provides power to the electrode array. Such a structure possesses specific electrical wave-guide properties which confines the RF radiation within a shielded zone while, at the same time, uniformly distributing power to the electrodes. The RF transition section will be designed during the next phase of the program in which the field test is to be conducted.

Matching Network

The RF matching network is a circuit capable of handling high power, and is used to obtain optimum conditions for power transmission between the RF power source and the load, which consists of the electrode array and soil. Optimum power transfer is obtained by matching the input impedance of the load to the output impedance of the power source. When these impedances are mismatched, the load does not absorb all of the generated power, instead some EM energy is reflected back to the power source. The reflected energy is dissipated as heat in the matching network and the power transmission cables. Mismatches are detected by measuring the forward power and the reflected power at the output of the RF power source. Variable components of the matching network are adjusted to reduce the reflected power to zero to obtain a matched condition.

Analysis of Electrode Array

The purpose of this analysis is to predict the input impedance of the load during various stages of the heating cycle. Soil dielectric properties which were measured as a function of the applied power frequency and soil temperature are utilized in this analysis. The predicted array input impedance is plotted on a Smith chart, in Figure 29. This information was used to determine the characteristics of the matching network needed at various portions of the heating cycle. It was concluded that a single matching network design will be utilized until the deposit temperature reaches 125° to 130°C, corresponding to an SWR of ~ 15:1, while the second design will be necessary from 130° to 160°C range (SWR < 35:1). The term SWR or standing wave ratio is a measurement of mismatch a given load impedance places on the transmission line. In this case, it is a measurement of the matching range required for the selected matches network design.

Estimate of Gas, Vapor, and Condensate Generation Rate

Based on the electrical analysis, a single fixed operating frequency of 6.78 MHz was selected to achieve the final temperature requirements. This frequency belongs to the ISM band frequencies allocated by the FCC for industrial, scientific, and medical instrumentation applications.

Gases and vapors formed during the treatment of the soil will be contained by the silicon rubber vapor barrier described in a previous section.

Table 22 gives information regarding the amount of water and contaminants present in the soil. It is estimated that the moisture content of the soil is 5% and the mass of heated soil is 69,000 lbs. Thus, 3450 lbs of water will be boiled up provided that migration of water from the surrounding soil is negligible.

The soil contains both hydrocarbon and chlorinated hydrocarbons. The hydrocarbons in the soil are weathered and degraded products of jet fuel, waste motor and lubricating oils. Thus the hydrocarbon layer of the condensate is expected to have a composition between that of aviation fuel or kerosene and lubricating oils. The chlorinated hydrocarbons are present in the soil because solvents were disposed off at the site prior to a fire training drill. The unburnt remnants of these materials are present.

It was estimated that the amount of hydrocarbons in the heated volume is 110 lbs. This is based on the analysis of soil samples performed by SAI Inc. It was found that the total concentration of hydrocarbons was in the range of 15 to 1590 ppm. The above estimate of the weight of hydrocarbons is

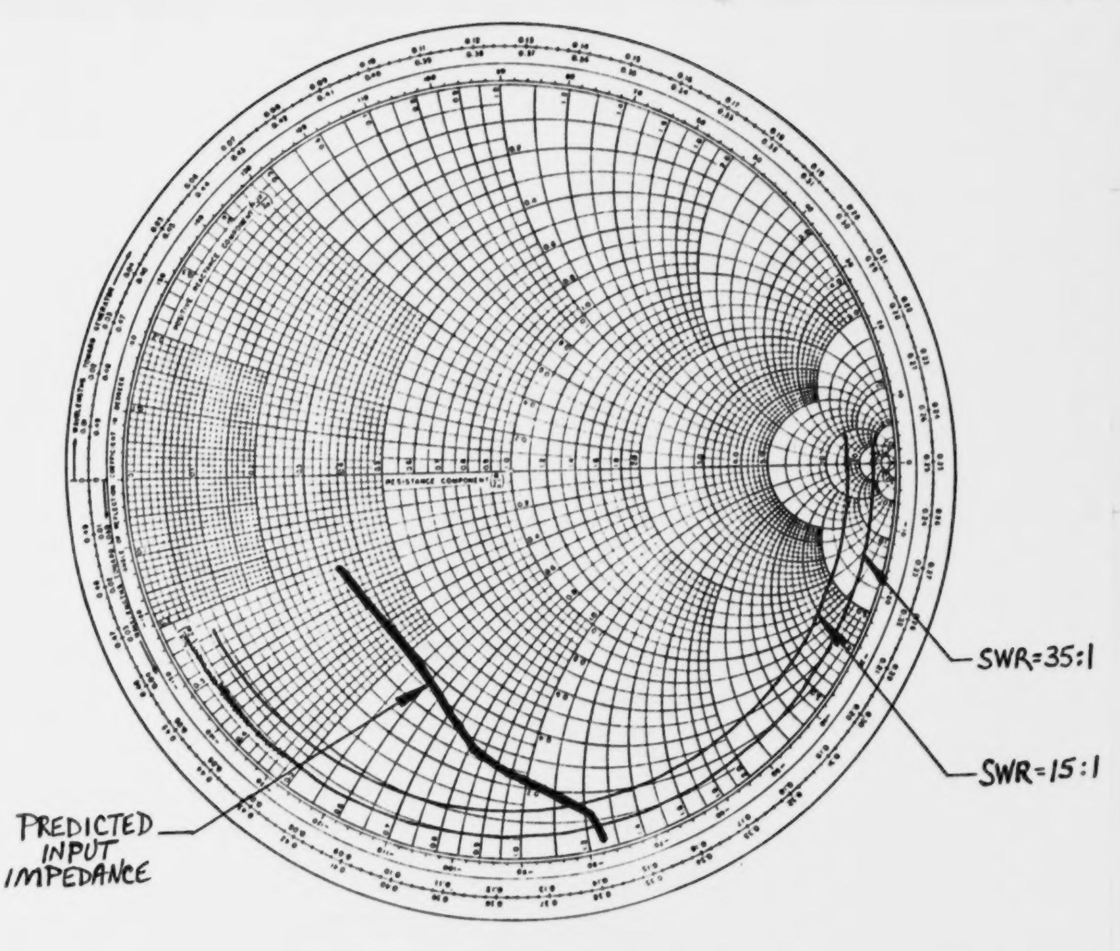

Figure 29. Predicted input impedance of the field test electrode array.

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based on the worst case assumption that the average concentration of hydrocarbons in the soil is 1600 ppm, and that the condensation efficiency is 100 percent.

The soil samples were also analyzed for dichloromethane, chloroform, 1,1,1-trichloroethane, and trichloroethylene. The total concentration of these materials was found to be in the range of 13 to 3450 ppb. It was estimated that the weight of chlorinated hydrocarbons in the heated volume is 0.21 lbs. This is based on the worst case assumption that the average concentration of these chemicals in the soil is 3000 ppb (3 ppm), and that the condensation efficiency is 100 percent.

The average rate of condensate collection is estimated to be 1.4 gal/hr after the average temperature of the heated soil reaches 50°C. From this point onward the rate is expected to be steady until the termination of the test. This estimate is based on the observed rate of condensate production in the tar sand in situ heating field experiments performed by Krystansky.[13]

The rate of hydrocarbon vapor and gas production can be estimated by assuming that the hydrocarbons are boiled up at a uniform rate from the time the soil reaches 50°C to the termination of the test. This time interval is estimated to be 11.5 days. Thus the rate of hydrocarbon vapor and gas production will be 10 lbs/day.

Similarly the rate of production of chlorinated hydrocarbon vapors may be estimated. Since the reported chlorinated materials are low boilers it will be assumed that most of these will be boiled in the time it takes the soil to be heated to 100°C and for all the water to be boiled out. It is estimated that this will take 6.5 days. Thus the rate of chlorinated hydrocarbon vapor production is estimated to be 0.03 lbs/day.

The maximum hydrocarbon concentration of the condensate water can be calculated for the worst case by making two assumptions. The first assumption is that the condensation efficiency is 100 percent. The second assumption is that the average concentration of the hydrocarbons in soil is the same as the highest concentration found by SAI in their soil sample analyses. This gives a concentration of 3.1% in the condensed water phase. Similarly, the concentration of chlorinated hydrocarbons in the condensate is estimated to be 60 ppm.

Collection and Treatment System

The collection and treatment system flow diagram is shown in Figure 30. On the left hand side of the figure an interface between the collection system and the vapor collection line placed inside the silicon rubber vapor barrier is shown. The gases and vapors will be sucked out of the collection zone using an induced draft blower shown in the far right of the figure. These gases, etc., will be cooled and condensed in a heat exchanger. The heat exchanger will use forced ambient air as the cooling fluid. It is proposed to use a heat exchanger capable of rejecting 41,000 Btu/hr. This is approximately twice the anticipated heat load, based on condensation and sub-cooling of 1.4 lbs/hr of superheated steam from 150°C to 27°C. The condensate will be separated from the uncondensed fraction and stored in 55-gal drums. The gases leaving the separator will pass through a carbon bed, a gas flow meter and into the blower.

All the condensate formed during the test will be collected and stored in closed drums. When a drum is receiving condensate, its head space will be vented to the inlet side of the heat exchanger to minimize emissions from the process.

The suction in the vapor line will be monitored at two different places as shown by the location of the pressure gauges. Sampling point will be provided in the gas lines at locations marked by SP.

SAMPLES AND DATA ACQUISITION

Various types of samples and test performance data will be acquired during the test. Four different types of samples and or data will be obtained. These are: soil samples from the heated volume before and after the test, two grab samples of heated soil when four days at 150°C have elapsed,

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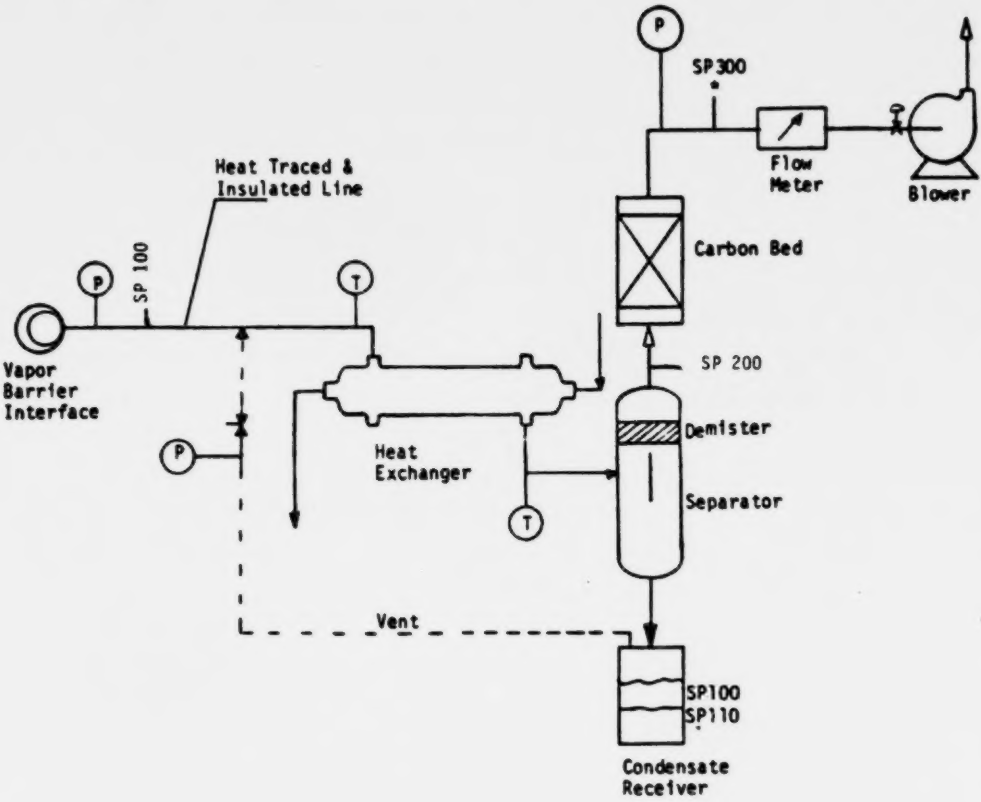
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SP300
Flow Meter
Blower
Heat Traced & Insulated Line
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Carbon Bed
Vapor Barrier Interface
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Demister
Heat Exchanger
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Separator
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Vent
SP100
SP110
Condensate Receiver

Figure 30. Gas and vapor handling system for Volk Field test.

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condensate samples, measurements and samples for determining process emissions, and test performance data. Each of the above activities are described in the following sub-sections.

Soil Samples

Soil samples will be taken from the test volume both prior to and after the test. The purpose of obtaining the samples is to make a reliable estimate of the average concentration level of the contaminants in the heated volume prior to and after the test. This information will be used to calculate the percentage removal from the soil. It is estimated that about 30 samples will be collected each time. The number and location of the sample points will be carefully selected in order to give a three dimensional spatial distribution of the contaminant concentration which is statistically significant. This data will be used to determine average concentration within the heated volume.

It is planned to obtain two grab samples from the heated zone after the soil has been maintained at an average temperature of 150°C for four days. The RF power will be switched off, the samples taken, and then the power turned on. The test will not be terminated until the results if these samples are available and reviewed. The purpose of this is to obtain an early estimate of the probable degree of decontamination before the test is terminated, and exhaustive sampling can begin. The intent is to preserve the option of extending the test duration after review of the two grab samples data.

Soil samples will be taken from the area which will be excavated to form the trench. These samples will be analyzed for heavy metals according to the EP-Toxicity Test Procedure, specified as EPA Standard Method 1310. The purpose of this is to determine whether the excavated soil is hazardous as per the EP-Toxicity test. This information will be used to determine how the excavated soil will be handled and disposed. Additional samples will be taken from the trenched area, before and after the test in order to determine the amount of contaminant migration outside the heated zone. These analyses will be similar to those performed on soil obtained from the heated zone.

The soil samples will be analyzed for moisture content, total and chlorinated hydrocarbons, and for the presence of certain marker compounds selected to represent each family of contaminants. In addition marker compounds will be selected to represent the boiling range of the chemicals present in the soil. For example, it is known that pentadecane is present in the soil. Pentadecane could be used as a marker for high boiling hydrocarbons. In addition, QA/QC samples as specified by the QA/QC plan will be taken from the field. These will include field blanks, replicates and duplicate samples. All the samples will be shipped to Chicago for analysis using GC/MS. The samples obtained from the field prior to the test will be analyzed before the test starts in order to ensure that enough samples have been obtained to characterize the site.

Condensate Samples

Condensate produced during the test will be collected in 55-gal drums. All the drums will be saved for separation of phases and treatment in Chicago. However, during the course of the test the rate of production and total volume of the condensate will be recorded. The volume fraction of the hydrocarbon layer will be determined as the test progresses. In addition, water and hydrocarbon layer samples will be taken for analysis. These layers will be analyzed for the same parameters as the soil samples. At least one sample per drum will be obtained for this purpose.

The purpose of condensate analysis is to estimate how much of the in-place contaminants have been recovered. Another purpose of the analysis is to determine whether the condensate is hazardous. As discussed previously, the concentration of chlorinated materials in the condensate is expected to be 60 ppm. Thus, the waste is not expected to be hazardous due to its chlorinated hydrocarbon content. The hydrocarbon constituents are expected to be 3.1 percent. Analysis of previously obtained soil samples have indicated that there are numerous (up to 15 to 20) hydrocarbon species present, thus, the concentration of any given species is not expected to exceed 10,000 ppm. Due to this reason it is possible that the condensate may not be considered hazardous due to its hydrocarbon content.

After the completion of the test, all the condensate drums will be shipped to IITRI's laboratories in Chicago. Here, the hydrocarbon layer will be separated from the water layer in all the drums. The hydrocarbon layer will be combined and analyzed. The water layers will be sampled and treated, if necessary, in a carbon bed for hazardous chemicals . Prior to disposal of the water layer, it may be necessary to adjust its pH to neutral. If the hydrocarbon layer is found to be hazardous then it will be sent to a licensed hazardous materials disposal facility for ultimate disposal.

Emission Monitoring Plan

Two types of emissions will be monitored during the test. These are emissions of RF energy from the test array and emissions of chemicals in the gas stream discharged from the carbon bed shown in Figure 30.

Monitoring of Electromagnetic Emissions--

Near and far field electromagnetic (EM) measurements will be made at and around the test area. Near field refers to the immediate vicinity of the test site. Far field refers to locations 0.25 to one mile from the test site. The far field locations will be selected in consultation with the base communications personnel. The purpose of these measurements is to ensure that the radiated RF power levels are below permissible FCC and Air Force standards and that no interference is generated with base communications.

These measurements will be made by turning on the RF power to the array at low levels prior to the test. The emission measurements will be made at two different low power levels. Should the level of emitted RF radiation exceed the permissible standards, then corrective action will be taken to reduce the emission levels to acceptable limits and base communication personnel's approval will be obtained. The near and far field measurements will be repeated shortly after the power input to the array reaches the normal operating levels around 30 kW and at regular time intervals throughout the test.

Monitoring of Gaseous Emissions--

Gases and vapors formed during the field test will be collected through the vapor collection line as shown in Figure 30. On this figure the location of three gas sampling points is indicated by the symbol SP. These points are the inlet to the heat exchanger, and the inlet and outlet of the carbon bed. The total gas flow rate leaving the carbon bed will be measured along with the total accumulated volume of gases sent to the blower.

The purpose of these analyses is to obtain quantitative data on total hydrocarbon and total emissions of certain selected chlorinated hydrocarbons in the gas streams. Another purpose of the field analyses of the gas stream is to obtain semi-quantitative information on how the concentration of the hydrocarbon components in the gas stream is changing with time. This information will be used as a measure of the progress and performance of the soil decontamination system as soil samples cannot be readily obtained from the heated zone while heating is in progress.

A portable FID probe will be inserted into the gas lines at the three locations shown in Figure 30 to determine the total hydrocarbon concentration of the gas stream. These measurements will be made at least six times during a 24 hour period. In addition, gas samples will be obtained in sample bottles to determine the quantity of chlorinated hydrocarbons in the gases leaving the carbon bed. The gas samples will be analyzed with a GC equipped with a ECD detector for the presence of selected chlorinated compounds mentioned previously.

In addition to these measurements, a lower explosion limit monitor will be used to determine the flammability of the atmosphere in the immediate vicinity of the test site, around the vapor barrier, and the transition zones.

Test Performance Data

Actual soil samples cannot be obtained while heating is in progress, therefore the decontamination performance of the system during the heating period will be indicated indirectly through the measurements of gas concentration, the production history of condensate, the fraction of hydrocarbon layer in the condensate and by mapping the temperature distribution in the heated zone. During the test the following parameters will be measure to control the heating and determine the performance:

- rate of production of condensate
- fraction of hydrocarbon vs aqueous layer in the condensate
- total gas flow rate leaving the carbon bed
- concentration of the gases at various points in the flow sheet (as shown by SP in Figure 30)

- temperature distribution in the soil
- total AC power consumed by the RF power source
- total AC power consumed by the treatment and collection system
- total RF power absorbed by the heated soil.

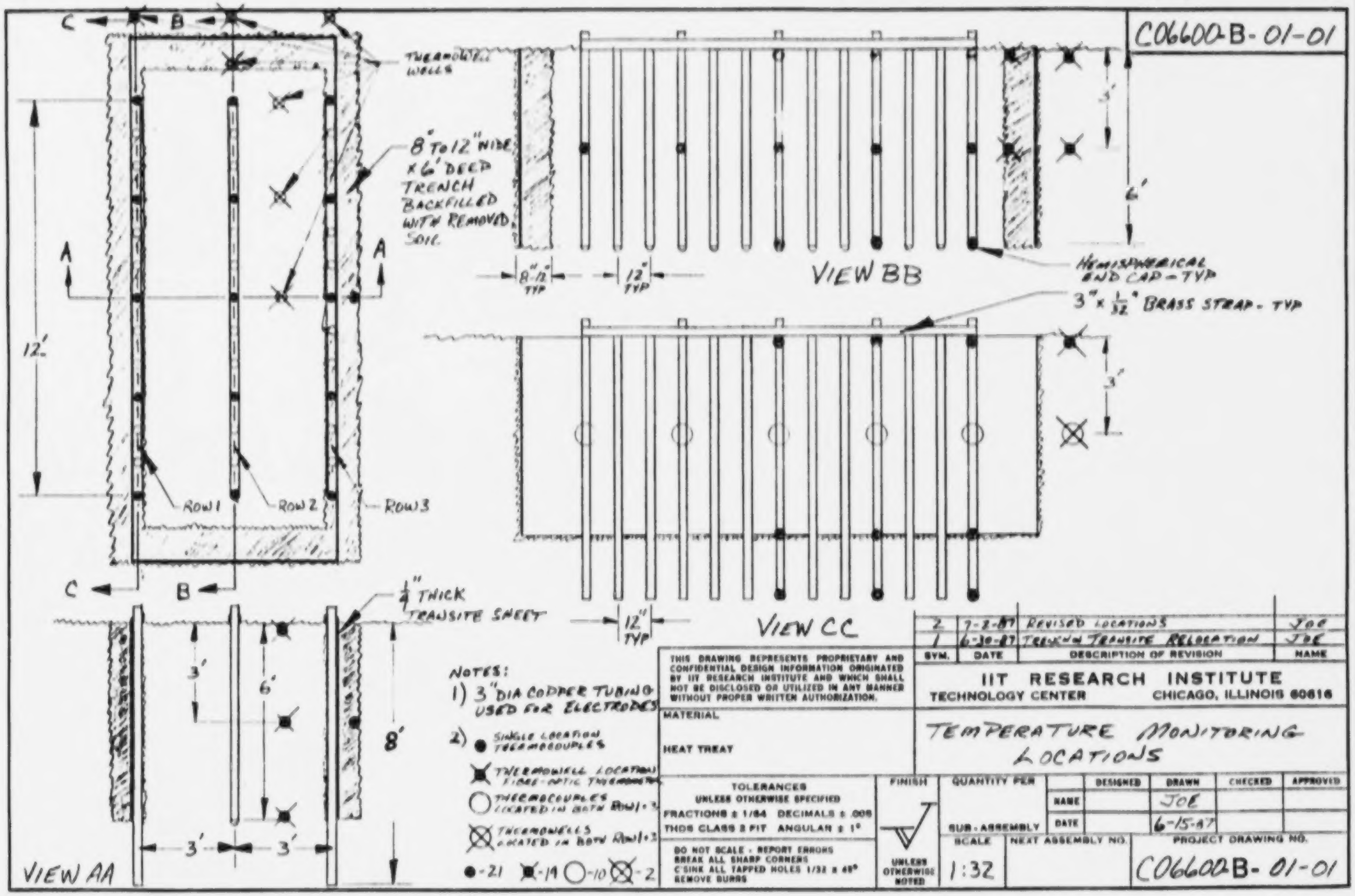
The soil temperature distribution will be charted in three dimensions by a combination of permanently imbedded thermocouples, by inserting thermocouples in thermowells and by inserting fiber-optic temperature sensors in thermowells. The three dimensional distribution of the various temperature measurement locations is shown in Figure 31. A total of 48 monitoring points is shown in this figure.

Table 23 summarizes the number of temperature measurement points available and their general location when RF power to the array is on and when it is off. Note that when the power is off, an additional 23 measurement points are added to the basic 25 measurement points when the power is on. The data from the 25 measurements points, when the power is on, will be available at any time during the test. Although these points will be monitored continuously, the data will be logged once an hour. The additional 23 points cannot be monitored or logged unless the RF power is turned off. It is proposed to log these data four to six times in a 24-hour period.

TABLE 23. NUMBER AND LOCATION OF TEMPERATURE MEASUREMENT POINTS

Location	RF Power On	RF Power Off
Row 1	14 T/C	14 T/C
Row 2	None	11 T/C
Row 3	5 T/C	5 T/C
Between Rows 2 and 3	2 F/O	9 F/O
In the Trenched Area	1 T/C	2 F/O
Outside Heated Zone and Trenched Areas	2 T/W	2 T/W 4 F/O
Total	25	48

T/C = Imbedded thermocouple
F/O = Thermowell for fiber optic temperature sensor
T/W = Thermowell for thermocouple.



C06600-B-01-01
THERMOWELL WELLS
8" TO 12" WIDE X 6' DEEP TRENCH BACKFILLED WITH REMOVED SOIL
A
A
12'
ROW 1
ROW 2
ROW 3
C
B
C
B
1/4" THICK TRANSITE SHEET
3'
6'
8'
3'
3'
VIEW AA
8"-12" TYP
12" TYP
VIEW BB
3'
6'
HEMISPHERICAL END CAP - TYP
3" x 1/32" BRASS STRAP - TYP
3'
12" TYP
VIEW CC
NOTES:
1) 3" DIA COPPER TUBING USED FOR ELECTRODES
2) ● SINGLE LOCATION THERMOCOUPLES
THERMOWELL LOCATION FIBRE-OPTIC THERMOMETER
○ THERMOCOUPLES LOCATED IN BOTH ROW 1 + 3
⊗ THERMOWELLS LOCATED IN BOTH ROW 1 + 3
●-21 -19 ○-10 ⊗-2
2 7-2-87 REVISED LOCATIONS JOE
1 6-30-87 TRENCH TRANSITE RELOCATION JOE
SYM. DATE DESCRIPTION OF REVISION NAME
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TECHNOLOGY CENTER CHICAGO, ILLINOIS 60616
MATERIAL
HEAT TREAT
TEMPERATURE MONITORING LOCATIONS
TOLERANCES UNLESS OTHERWISE SPECIFIED
FRACTIONS ± 1/64 DECIMALS ± .005
THDS CLASS 2 FIT ANGULAR ± 1°
DO NOT SCALE - REPORT ERRORS
BREAK ALL SHARP CORNERS
C'SINK ALL TAPPED HOLES 1/32 x 45°
REMOVE BURRS
FINISH
UNLESS OTHERWISE NOTED
QUANTITY PER
SUB-ASSEMBLY
SCALE 1:32
NEXT ASSEMBLY NO.
DESIGNED DRAWN CHECKED APPROVED
NAME JOE
DATE 6-15-87
PROJECT DRAWING NO.
C06600-B-01-01

Figure 31. Temperature monitoring locations for the Volk Field test.

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APPENDIX A

ANALYSIS OF SOLVENTS AND JET FUEL IN SANDY SOIL

In this appendix, the procedures for the analyses of tetrachloroethylene, chlorobenzene, and jet fuel in soil are described. Analysis of these contaminants in soil is a two-step procedure. The first step consists of extraction and removal of the contaminant from the soil into an organic solvent. The second step consists of analysis of the extract phase for the contaminant of interest.

During the course of this program, distillates were produced by condensation of vapors formed during the thermal-treatment experiments. After drying, the distillates were analyzed for contaminants using procedures of the second step mentioned above.

For all experiments, the extraction step was performed by steam distillation of the soil in a Nielson-Kryger distillation apparatus. But two different methods were used for the analysis of distillate depending upon the type of contaminants present.

When the only contaminant present in soil was tetrachloroethylene, the extracts as well as the distillates were analyzed on a gas chromatograph equipped with an electron capture detector (ECD). When tetrachloroethylene and chlorobenzene were present together or when jet fuel was present in soil, the extracts as well as distillates were analyzed on a GC/MS system.

NIELSON-KRYGER STEAM DISTILLATION-EXTRACTION OF SOIL

Equipment

A Nielson-Kryger steam distillation condenser (sold by Ace Glass, Inc.); 500 ml Pyrex® round-bottom flask, disposal glass pipettes for preparing Tenax® traps, prewashed Pyrex® glass wool plugs.

Reagents

TA grade, 60/80 mesh Tenax®; pesticide grade iso-octane; HPLC grade hexane, anhydrous sodium sulfate, ACS grade; and hydrocarbon free distilled water.

Sample Preparation

Contaminated soil needs no special preparation prior to steam distillation.

Procedure

Steam distillation of the soil was performed to remove the contaminants in the soil and to transfer them to a liquid phase that could then be analyzed on a gas chromatograph (GC) using an electron capture detector (ECD), or a GC/MS system.

Approximately 75 gms of the soil sample was placed in the 500 ml round bottom flask, 250 ml of hydrocarbon (HC) free water was added and the flask was attached to the Nielson-Kryger condenser as shown in Figure A-1. The condenser was charged with approximately 10 ml of HC free water followed by approximately 10 ml of hexane. The two liquids separate into two phases in an annular zone in the lower part of the condenser. The heavier water phase fills the liquid withdrawal tube and partially fills the water overflow tube. A disposable glass pipet filled with approximately 1 gm of Tenax® was attached to the condenser opening at the top.

When the water, soil, and contaminant mixture is brought to boil in the flask, the vapors rise up through the vapor-riser and condense on the walls of the condenser. The condensate collects in the annular space which was prefilled with hexane/water. The condensate separates into two phases with simultaneous extraction of the contaminant into the hexane phase. As the steam distillation proceeds, the water layer increases in volume until it begins to reflux through the overflow tube. The steam distillation was performed for a period of 16 hours on each soil sample, at the end of which the heating was discontinued and the apparatus allowed to cool to room temperature.

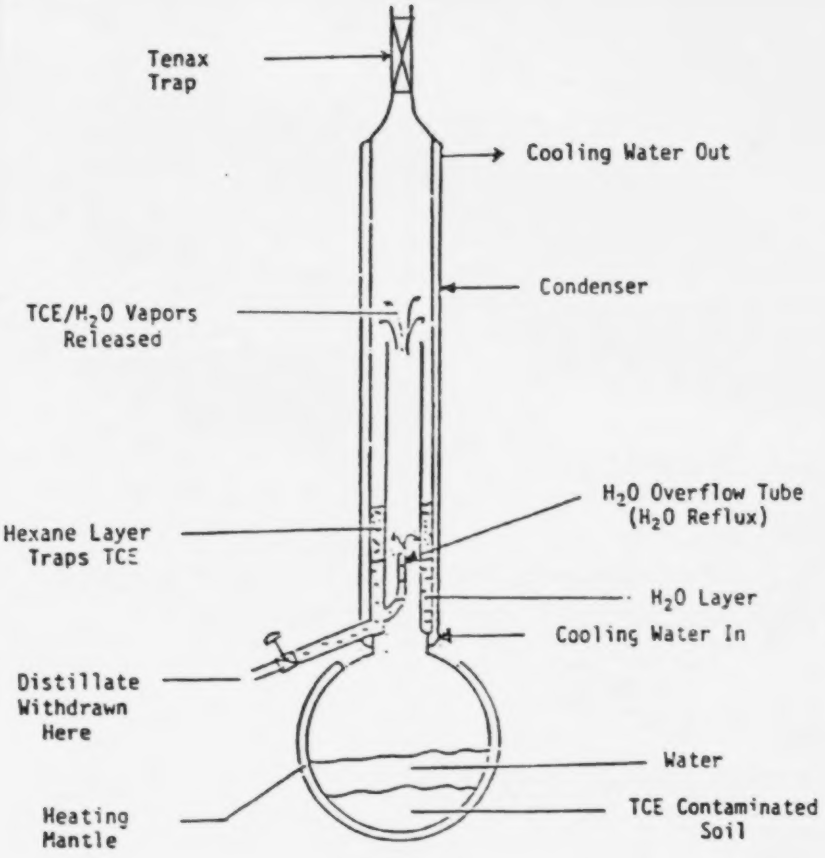
Tenax Trap
Cooling Water Out
Condenser
TCE/H_2O Vapors Released
H_2O Overflow Tube (H_2O Reflux)
Hexane Layer Traps TCE
H_2O Layer
Cooling Water In
Distillate Withdrawn Here
Water
Heating Mantle
TCE Contaminated Soil

Figure A-1. Nielson-Kryger steam distillation apparatus.

TYPING GUIDE SHEET

The water and hexane phase were recovered into a separatory funnel. The Tenax® trap was removed from the condenser and flushed with pure hexane (10 ml) to remove any trapped contaminant. The condenser was rinsed with water and hexane to remove any unrecovered droplets of water. The washings were also added to the separatory funnel. After allowing the two phases to separate, the water phase was drained from the funnel and the remaining hexane phase was combined with the hexane from the Tenax® wash and dried through a bed of anhydrous sodium sulfate. The dried hexane phase was brought up to a volume of 100 ml in a volumetric flask. Two to three drops of triple distilled mercury was added to the recovered extract to remove sulfur impurities.

DETERMINATION OF TETRACHLOROETHYLENE RECOVERY EFFICIENCY

The purpose of this evaluation was to determine what fraction of tetrachloroethylene originally contained in soil could be recovered during steam distillation and the subsequent sample preparation steps. The recovery of tetrachloroethylene was expected to be less than 100 percent for several reasons: (1) strong irreversible adsorption of tetrachloroethylene on the soil, (2) evaporative losses, and (3) sample loss during transfer, phase separation, drying, etc.

Of the three reasons mentioned above, adsorption of tetrachloroethylene in soil was expected to account for most of the recovery losses. Evaporative losses were minimized in the proposed techniques by two precautions: the use of Tenax® traps to minimize loss of uncondensed tetrachloroethylene through the condenser and the use of ice baths to chill the distillate during preparatory steps like phase separation, drying, etc. Sample losses during distillate transfer, phase separation, drying was minimized by thoroughly rinsing all glassware with fresh hexane. The rinsate was combined with the distillate prior to the drying step.

Steam distillation of tetrachloroethylene and water mixture in the absence of soil showed essentially the same recovery efficiency as for steam distillation of spiked soil. Thus, irreversible adsorption of tetrachloroethylene on the sandy soil used in this study was presumed to have negligible effect upon recovery efficiency.

The recovery efficiency for tetrachloroethylene was determined by the steam distillation of spiked soil. The recovery efficiency was found to range from 86 to 107 percent. In Table A-1 the data on recovery efficiency is presented. In Figure A-2 the recovery efficiency is plotted as a function of true concentration of tetrachloroethylene in soil. The data in this figure show that the recovery efficiency is independent of the tetrachloroethylene concentration in soil. An average recovery efficiency of 97.1 percent was obtained.

Procedure for Spiking Soil

Spiked soil samples were prepared by adding to the soil a known volume of a tetrachloroethylene solution in iso-octane. The concentrations of the solution were determined by GC analysis. Each recovery efficiency experiment was performed using 75 gms of soil containing 5.7 percent moisture in a 500 ml Pyrex® glass round bottom flask. A known volume of spiking solution was added to the soil, the flask was sealed and the spiked soil was tumbled for a period of 3 hours by attaching the sealed flask to a rotovap. To prevent vaporization of tetrachloroethylene during tumbling the rotating flask was placed in an ice bath. After 3 hours of tumbling the flask was attached to the Nielson-Kryger distillation condenser. The recovery experiments were performed in the same flask in which the soil was spiked and tumbled.

The steam distillation and sample preparation were performed according to the procedure described above.

GC/ECD PROCEDURE FOR EXTRACT AND DISTILLATE ANALYSIS

As mentioned earlier, two different procedures were used for the analysis of extracts and distillates. The GC/ECD procedure was used when the only contaminant present in soil was tetrachloroethylene; when chlorobenzene or jet fuel was present a GC/MS procedure was used.

TABLE A-1. RECOVERY EFFICIENCY OF TETRACHLOROETHYLENE FROM SPIKED SOIL[a]

No. of Times Extracted	No. of Times Analyzed on GC	Concentration of Spiked Soil, ppm 1190	990	910	500	460	250	59	30	0.094
1	1	97.0	101.1	95.6	87.7	100.2	98.9	97.6	107.2	105.6
	2	93.9	99.9	106.4	97.3	95.8	95.3	98.0	103.8	95.0
	3	95.4		96.7		97.7	95.4			--
	4			94.4		97.9				--
2	1	95.6	98.5				99.7		97.5	
	2	92.4	97.7				96.2		97.3	86.7
	3	96.3					95.0			90.4
	4									--
Average		95.1	99.3	98.3	92.5	97.9	96.8	97.8	101.5	94.4
Std deviation		1.68	1.51	5.50		1.80	2.03	--	4.88	8.19
% Std deviation		1.8	1.5	5.6		1.8	2.1		4.8	8.7
n		6	4	4	2	4	6	2	4	4

[a] Tyndall AFB soil steam distilled

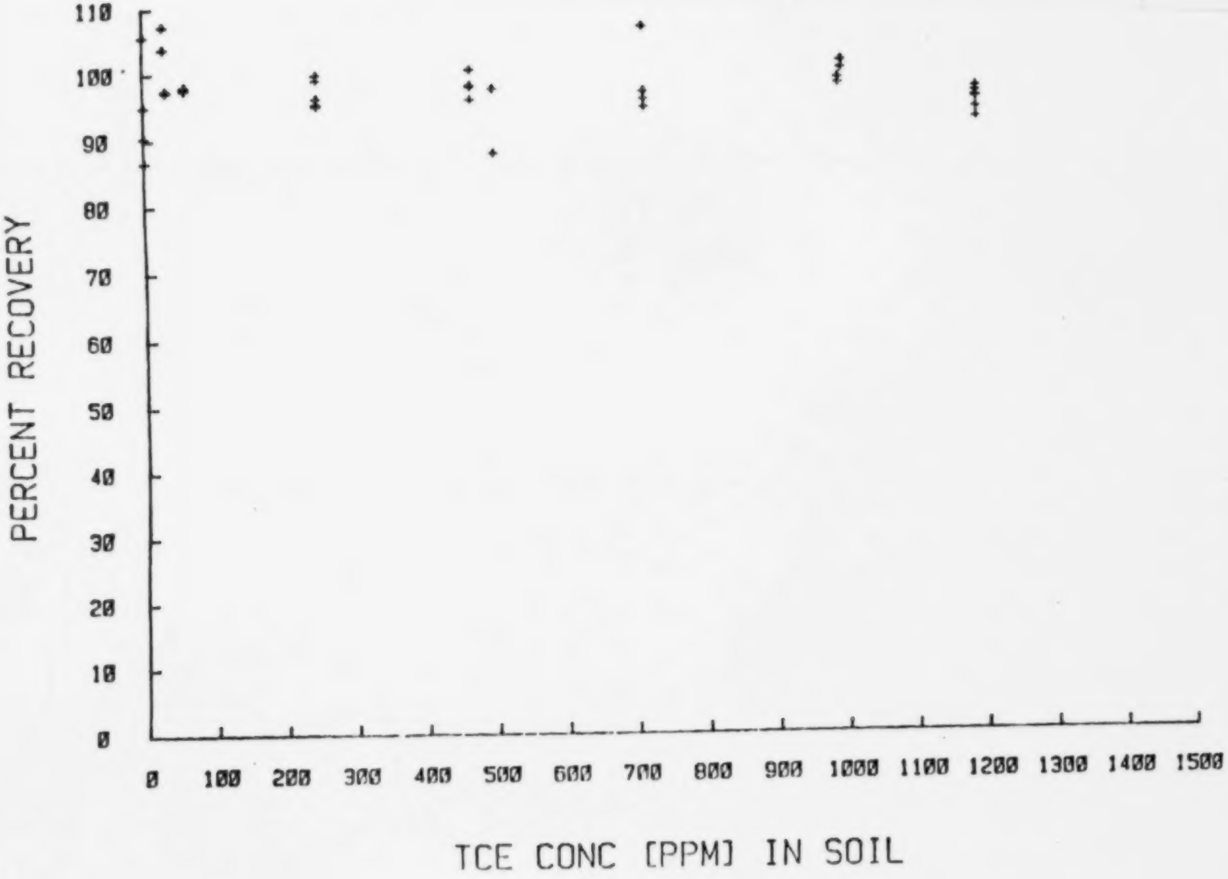

Figure A-2. Tetrachloroethylene recovery efficiency by steam distillation.

Equipment

A Hewlett-Packard 5840 gas chromatograph equipped with a Ni^{63} electron capture detector was used for the analysis. The separation was performed on a 2-meter long, 1/8-inch I.D. stainless steel column packed with 4 percent OV-101 supported on 80/100 mesh chromosorb G, AW-DMCS supplied by Supelco, Inc. The GC operating conditions are summarized in Table A-2.

TABLE A-2. GC OPERATING CONDITIONS

Temperatures:	
Oven	70°C (isothermal)
Injector	175°C
Detector	200°C
Carrier Gas:	5% CH_4 in 95% Argon 20 ml/min
Analysis time	25 minutes
Average retention time of tetrachloroethylene	5.8 ± 0.1 minutes

Sample Injection Procedure

Approximately 1.5 to 4.0 μl of the prepared sample (or calibration standard) was injected into the GC with a 10 μl syringe. The solvent flush injection method (1.5 μl air, 2 μl of hexane, 1 μl air, sample, 1.0 μl air) was used. Between injections the syringe was cleaned by rinsing 10 times each in three different bottles of MeOH and five times each in two different hexane bottles.

Calibration Procedure

The GC was checked with three different calibration standards every day. The area response was compared with the full calibration curve to check for deviations and linearity. If the daily GC check showed a deviation of more than 10 percent, then the GC was recalibrated. Fresh calibration standards were prepared every week. When not in use, the calibration standards were kept under refrigeration at a temperature of -20°C. Before use, each standard was allowed to warm up to room temperature and checked for integrity and volume loss.

Calibration standards were prepared by volumetric dilution of a stock solution prepared gravimetrically from 99.9 percent HPLC grade tetrachloroethylene. Fresh stock solutions were prepared on a monthly basis.

Solvent blanks were performed on the pesticide grade iso-octane. These blanks showed a small response at the same retention time as that of tetrachloroethylene. It was determined that for soil experiments at 1000 ppm level, the solvent blank concentration would be a factor of 400 less than that of the most dilute sample to be analyzed. For this reason, iso-octane was used as a solvent. However, in the course of the program, it was decided to perform experiments with soil containing 10 ppm contaminants. It was determined that for such experiments iso-octane could not be used as a solvent for preparing calibration standards. It was estimated that the solvent blank concentration would be less than the response of the most dilute sample by only a factor of 15. Therefore, various solvents were screened until HPLC grade cyclohexane was found to give no interfering response with tetrachloroethylene. Solvent blanks were also performed on other solvents used in this program such as hexane and methanol. It was verified that these materials did not interfere with tetrachloroethylene.

Multipoint calibration curves were obtained by injection of prepared standards and plotting the mass of tetrachloroethylene injected against the area response on the GC.

Figure A-3 shows a typical calibration curve for standards prepared in iso-octane. A second order polynomial was fitted to the data. The equation of the fitted curve was:

$$Y = 2.59\ x^2 + 12.7\ x + 0.0624 \qquad \text{(A-1)}$$

where Y is the amount of tetrachloroethylene injected, nanograms

x is the scaled area response obtained by dividing the actual area response by 10 .

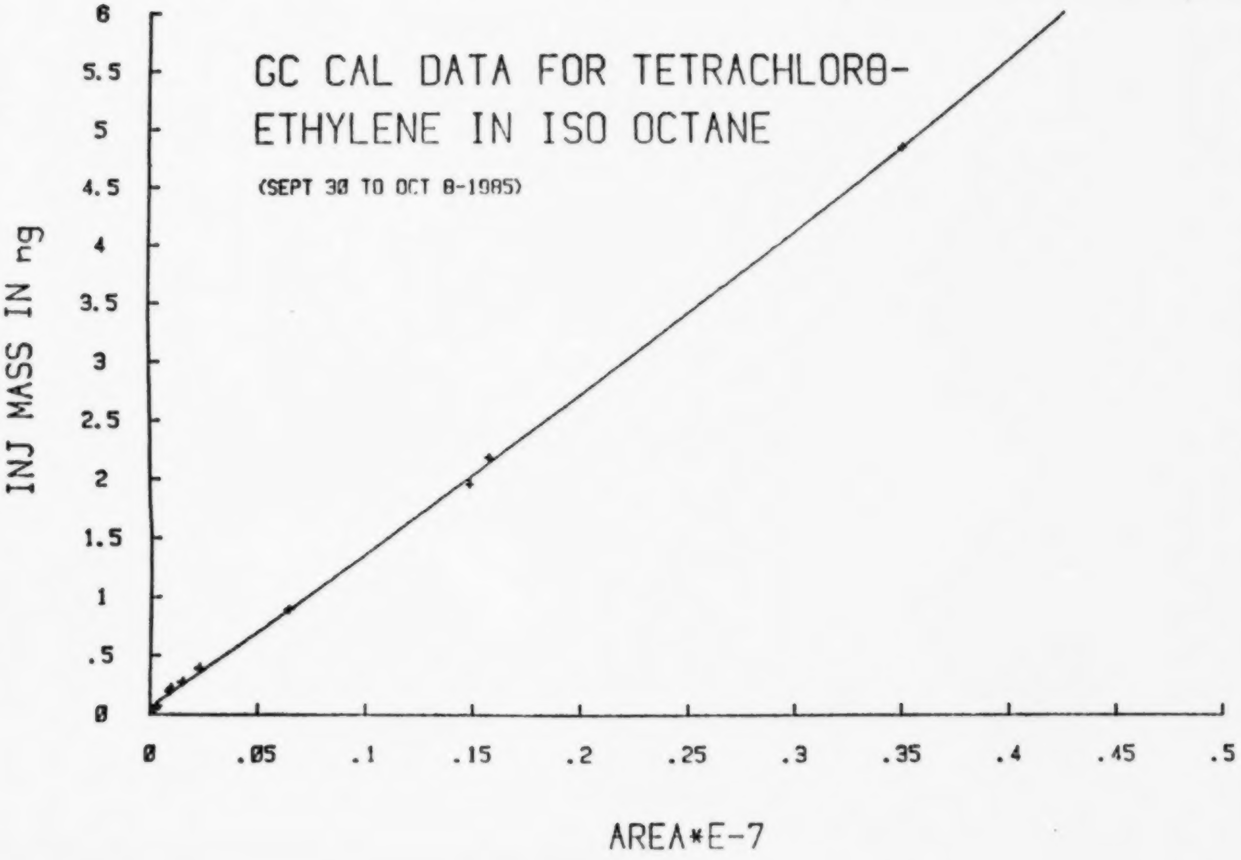

Figure A-3. GC calibration data for tetrachloroethylene in iso-octane.

The r^2 value for the above fit is 0.99945.

Figures A-4 and A-5 give calibration curves for standards prepared in cyclohexane at high and low levels, respectively. The data from each of these calibration curves was fitted to second-order polynomials.

The equation obtained for the high-level calibration data of Figure A-4 was:

$$Y = 5.38\ x^2 + 10.40\ x + 0.115 \qquad \text{(A-2)}$$

The r^2 value for this fit is 0.9972.

The equation obtained for the low-level calibration data of Figure A-5 was:

$$Y = -89.4\ x^2 + 16.63\ x + 0.0122 \qquad \text{(A-3)}$$

The r^2 value for this fit is 0.9916.

Correlation of high and low level data separately allowed simple regression equations to be fitted to the data while still minimizing the error of the correlations.

Calculation Procedure

The following procedure was used for calculating the concentration of tetrachloroethylene in soil. This was done by analyzing the concentration of tetrachloroethylene in the distillate obtained from steam distillation of the soil. The total weight of tetrachloroethylene recovered in the distillate was corrected by the weight of soil extracted to obtain the apparent concentration in the soil. A recovery efficiency correction was used to obtain the true concentration of tetrachloroethylene in soil.

Let the area response of the tetrachloroethylene peak be A_x when V_x μl of a prepared soil extract (obtained by the steam distillation of a soil sample) is injected. Then the concentration of the tetrachloroethylene in the soil can be calculated by the following equations.

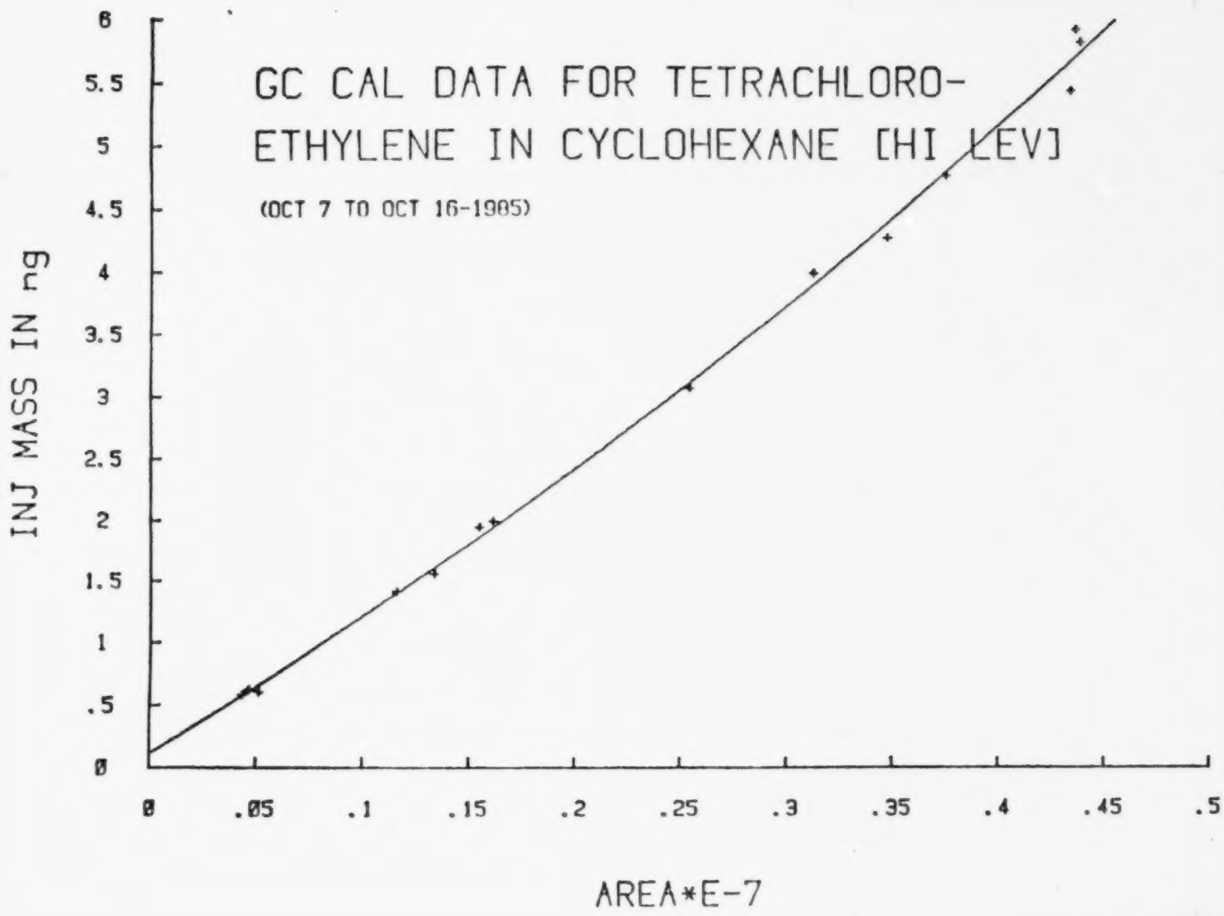

Figure A-4. GC calibration data for tetrachloroethylene in cyclohexane (high levels).

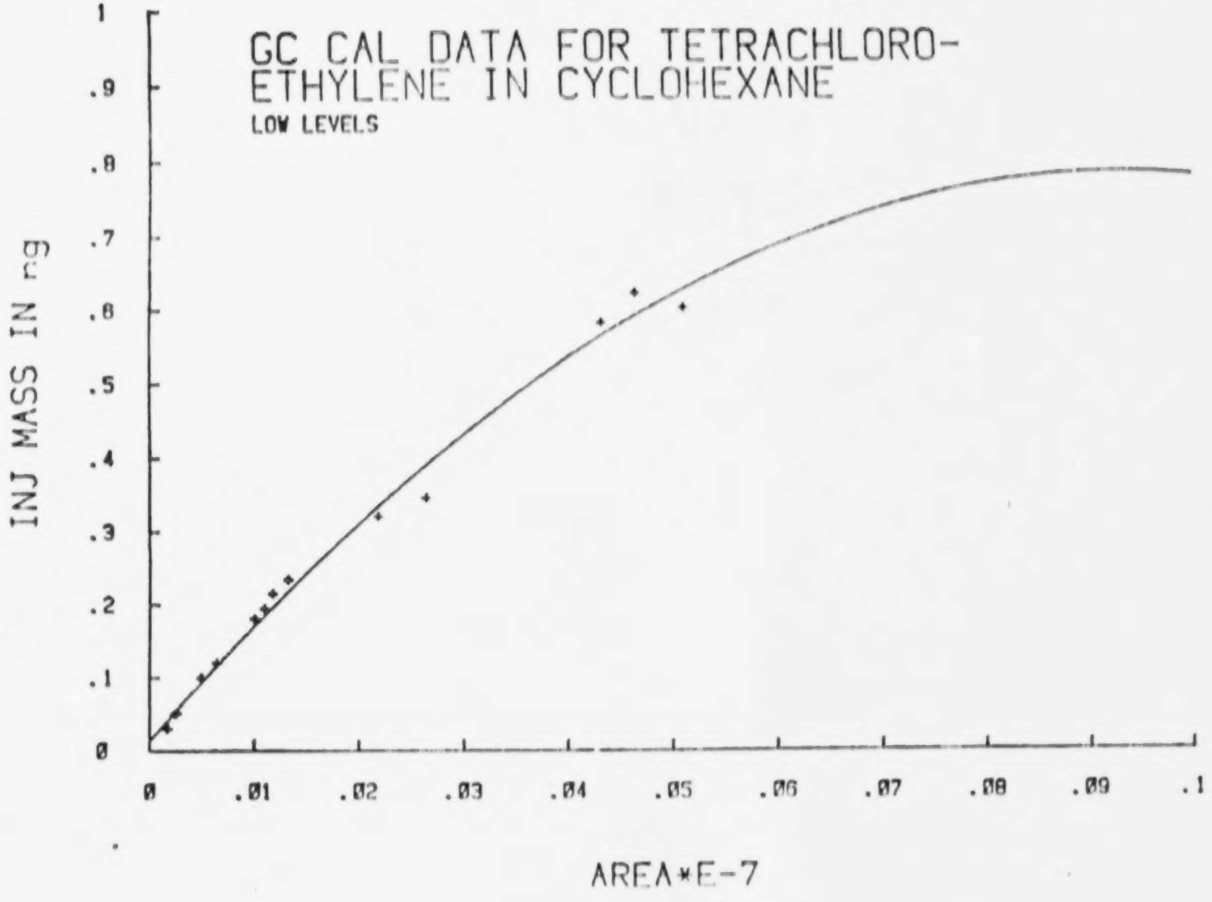

Figure A-5. GC calibration data for tetrachloroethylene in cyclohexane (low levels).

$$C_x = \frac{Y_x}{v_x} \quad \frac{(DF) \quad V_e}{M_s} \quad (\frac{1}{\zeta}) \quad \text{ppm} \tag{A-4}$$

$$Y_x = \sum_{i=0}^{3} a_i \, A_x^{\,i} \tag{A-5}$$

where C_x = concentration of tetrachloroethylene in soil, ppm

Y_x = weight of tetrachloroethylene injected on column, ng

V_x = volume of sample injected, µl

DF = dilution factor if prepared sample is diluted before injection

V_e = volume of extract made by steam distillation, ml

M_s = weight of soil extracted, gms

ζ = recovery efficiency

a_i = parameters of the second order polynomial fitted to the GC calibration curve (obtained from equation 1, 2, or 3)

A_x = scaled area response of the tetrachloroethylene peak.

GC/MS ANALYSIS OF EXTRACTS AND DISTILLATES CONTAINING CHLOROBENZENE AND TETRACHLOROETHYLENE

The purpose of this experiment was to analyze the soil sample extracts for the presence of TRCE and CBZ, and to quantify the amount detected. This procedure can be carried out by using a gas chromatograph with an electron capture detector. Initially, this method was used for the analysis but there were difficulties in the detection of CBZ due to its relatively low electron capture response. Therefore, combined gas chromatograph/mass spectrometry (GC/MS) was chosen as the analysis technique.

Equipment

Samples and standards were analyzed using combined capillary column GC/MS. The gas chromatograph, a Hewlett-Packard 5890, was equipped with a 30 m x 0.33 mm i.d. BP1 bonded phase vitreous silica (S.G.E. Australia) capillary column. Samples were injected in the splitless mode, with the column programmed from 40°C (isothermal for 5 min) up to 220°C at 4°/min. The carrier gas (He) flow rate was set at 0.83 ml/min. The column was coupled directly to the ion source of the mass spectrometer, a HP 5970A mass selective detector (MSD). The MSD was operated in the selected ion monitoring (SIM) mode.

Two masses for each of the compounds of interest, TRCE and CBZ, were selected for monitoring during the SIM experiment. The masses monitored for TRCE were 163.8 and 165.8 amu and 77.0 and 111.9 amu for CBZ. The process leading to the selection of these masses involved analyzing a standard solution containing TRCE and CBZ in the cyclic scan mode, scanning the mass range from m/e 34 to m/e 200. The mass spectrum of each compound was examined and the two masses having the highest intensity were selected for the SIM mode.

The parameters for the SIM experiment included setting up two time windows (one window for each of the 2 sets of masses). The times chosen for these windows were based on the retention times of the two compounds. The dwell time on each mass was 200 msec. The total cycle time was 0.5 sec/cycle. The multiplier applied voltage was set at 2.0 KeV. The data acquired were stored using the HP 9816S computer equipped with a 15 Mbyte hard disc drive. (The HP 9816S is the controller for the GC/MS system. It also receives the data from the detector and presents the data in a suitable form to the user.)

Quantification

An external standardization method was chosen in order to quantify the experimental samples submitted for analysis. A series of standard solutions in the concentration range 0.06 to 6.0 ng/ul for TRCE and CBZ was prepared. These solutions were used to calibrate the instrument. A calibration curve, similar to the one illustrated in Figure A-6, was generated and used to determine the levels of TRCE and CBZ present in the experimental samples. To ensure instrument stability, a calibration standard was analyzed each work-day prior to sample analysis. If the value of the calibration standard was not within 10% of the working curve, then the instrument was recalibrated. The experimental sample concentration for each compound was determined from the calibration curve, using the standard program in the data system.

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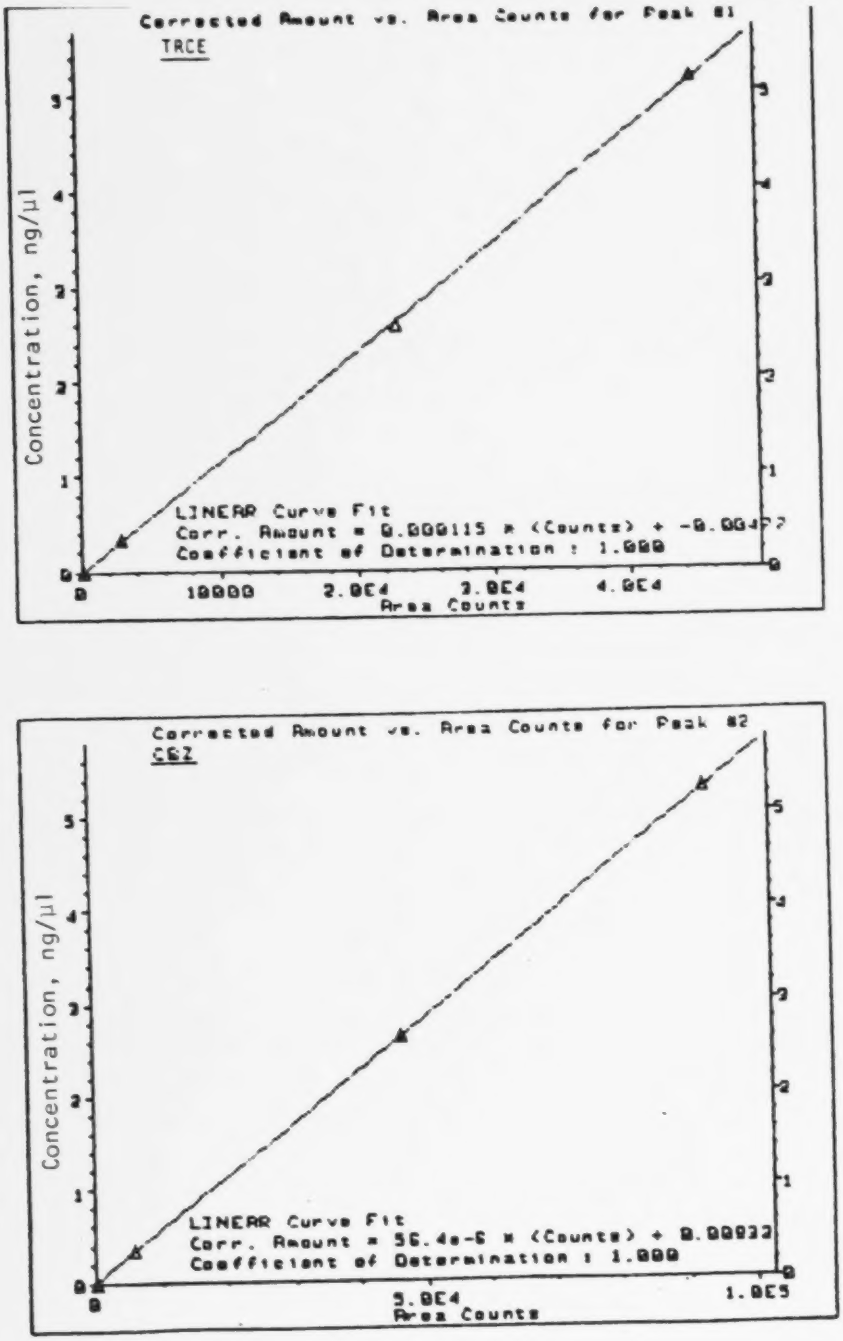


Figure A-6. Sample calibration curve for: (#1) tetrachloroethylene (TRCE) and (#2) chlorobenzene (CBZ).

Quality Control

Quality control samples were periodically submitted along with the experimental samples for analysis in order to verify that the results reported were reliable.

A summary of the results for the analysis of one set of QC samples is in Table A-3. The results reported are based on one analysis of each sample. The values obtained based on the analysis results between concentration range 6.0 to 0.20 ng/ul are within a 10% relative error. The percent relative error is higher for those concentrations which begin to fall outside the linear range of the calibration curve. Also, at the lower end of the calibration range, the concentrations begin to approach the lower detection limits of the instrument. In order to improve the results of the values obtained at the low concentration level, an additional calibration curve was prepared in the concentration range 0.2 to 0.02 ng/ul. All other samples were prepared to lie within the linear range of the calibration curve.

Detection Limits

The detection limit is estimated to be 0.038 ng/ul for TRCE and 0.020 ng/ul for CBZ. These concentrations are based on a peak which is assumed to be 2.5 x the background noise. Converted to soil basis, this corresponds to 51 ppb for tetrachloroethylene and 27 ppb for chlorobenzene.

GC/MS PROCEDURE FOR EXTRACTS AND DISTILLATES CONTAINING JET FUEL

The purpose of this analysis was to determine the concentration of total aromatics, total nonaromatics, toluene and pentadecane in extracts obtained by Nielson-Kryger steam distillation of soil containing jet fuel.

Toluene was chosen to represent the aromatics present in the samples, while pentadecane ($C_{15}H_{32}$) was selected to represent the high boiling compounds. Combined gas chromatography/mass spectrometry (GC/MS) was used as the analysis technique.

TABLE A-3. RESULTS OF QUALITY CONTROL SAMPLE ANALYSES

Sample	GC/MS Code	Expected Amt TRCE, ng/ul	Calculated Amt TRCE ng/ul	% Error	Expected Amt CBZ, ng/ul	Calculated Amt CBZ, ng/ul	% Error
VS10-27-86 I	TB61028	6.195	5.590	9.76	4.340	3.740	13.8
VS10-27-86 II	TB71028	2.478	2.500	0.89	1.736	1.650	4.95
VS10-27-86 III	TB21029	0.620	0.611	1.45	0.434	0.405	6.68
VS10-27-86 IV	TB91028	0.248	0.264	6.45	0.174	0.182	4.60
VS10-27-86 V	TB41029	0.0991	0.127	28.1	0.0694	0.0864	24.5
VS10-27-86 VI	TB101029	0.0496	0.0665	34.1	0.0347	0.0487	40.3

(Note: TRCE = tetrachloroethylene, CBZ = chlorobenzene)

$$\% \text{ Error} = \frac{\text{Expected Amt} - \text{Calculated Amt}}{\text{Expected Amt}} \times 100\%$$

Equipment

Samples and standards were analyzed using combined capillary column GC/MS. The gas chromatograph, a Hewlett-Packard (HP) 5890, was equipped with a 30 m x 0.33 mm i.d. BPI bonded phase vitreous silica (S.G.E. Australia) capillary column. Samples were injected in the splitless mode, with the column programmed from 40°C (isothermal for 5 min.) up to 220°C at 6°/min. The carrier gas flow rate was set at 0.83 ml/min. The column was coupled directly to the ion source of the mass spectrometer, a HP 5970A mass selective detector (MSD). The quadrupole mass filter of the MSD was scanned from m/e 20 to m/e 250 at a scan rate of 0.9 scans/sec during the run. The multiplier applied voltage was set at 1.8 KeV. The data acquired were stored using the HP9816S computer equipped with a 15 M-byte hard disc drive.

Quantification

An internal standardization method was used to quantify the experimental samples. The soil extracts were spiked prior to extraction with a standard mixture containing the surrogate standards, toluene-d_8, octane-d18, and decane-d22, and also the internal standard, m-fluoroiodobenzene (FIB). After extraction, the hexane extract was spiked with the internal standard 4-fluoro-2-iodotoluene (IFT). An aliquot of this extract was analyzed by GC/MS. The distillate samples were spiked with the internal standard IFT immediately prior to analysis.

Relative response factors (RRF) were determined from the analysis of a standard solution containing the internal standards and the surrogate standards (toluene-d_8 and decane-d22) representative of the two target compounds of interest. Response factors were calculated from the following equation:

$$RF = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (Q_x)}$$

where A_x = total peak area of the analyte

A_{is} = total peak area of the specified internal standard (IFT)

Q_{is} = concentration of the internal standard (ng/µl) (IFT)

Q_x = concentration of the analyte in the standard (ng/µl)

The standard solution was analyzed in duplicate and an average response factor was generated for each compound of interest. The values are summarized in Table A-4.

TABLE A-4. AVERAGE RESPONSE FACTORS FOR CALIBRATION COMPOUNDS

Compound	Average Response Factor With Respect to IFT
Toluene-d_8	1.45 ± 0.01
Decane-d_{22}	1.96 ± 0.01

The average response factors for toluene-d_8 and decane-d_{22} were used in the quantification of toluene and pentadecane present in the samples.

The quantification of the total aromatics was based on the total area sum of those peaks with the characteristic m/e 91 in the full GC/MS profile. This area response value was subtracted from the total area response for the entire chromatographic envelope to determine the nonaromatic contributions to the amount of material present in the soil.

Recovery Efficiencies

The recovery efficiency for the soil extraction experiments was determined by comparing the actual amount of the surrogate standards found in the samples to the expected amount based on the known amount spiked onto the soil sample prior to extraction. The actual amount of the surrogate standard was determined from the relationship:

$$\text{ng}/\mu\text{l} = \frac{(A_i)\ (I_s)}{(A_{is})\ (\text{RF})}$$

where A_i = peak area of the surrogate

A_{is} = peak area of the internal standard

I_s = the concentration of internal standard in the sample (ng/µl)

RF = the response factor determined from the standard analysis (reported in Table A-4)

The actual amount was then compared to the expected amount and a percent recovery was calculated. The results are summarized in Table A-5.

TABLE A-5. RECOVERY EFFICIENCIES FOR THE SURROGATE STANDARDS TOLUENE-d_8 AND DECANE-d_{22}

	Initial Soil		Treated Soil	
Expt. No.	Toluene-d_8	Decane-d_{22}	Toluene-d_8	Decane-d_{22}
6	58%	96%	93%	90%

Note: Recovery efficiencies were not calculated for Experiment 5 because these soil samples were not properly spiked with the surrogate standards.

Good peak response was obtained for the spent soil samples.

Detection Limits

The detection limit was defined as the minimum detectable concentration required to produce a signal 2.5 times the average background signal. Based on the signal response for the internal standard IFT, the detection limit was determined to be 4 ng/µl.

APPENDIX B

ANALYSIS OF AROCLOR 1242 IN SOIL AND CONDENSATE

Thermal recovery experiments were performed to determine the feasibility of removing Aroclor 1242 from soil by vaporization and the action of steam sweep provided by injecting water in soil maintained above 100°C. The decontamination efficiency was determined by the analysis of soil samples after the treatment. In order to establish the mass balance, condensate produced during the experiment was extracted with hexane. The reactor and gas lines were rinsed with hexane. Both the extract as well as the rinsates produced were analyzed for Aroclor 1242. In this appendix the procedures for the extraction of soil, extraction of condensate with hexane and the analysis of the prepared samples are described.

SOXHLET EXTRACTION OF SOIL

The Soxhlet extraction procedure was used on the soil after the decontamination experiment as well as on spiked soil samples to determine extraction efficiency. This procedure is a simplified version of the extraction method described in Appendix C in which Soxhlet extraction of soil containing KPEG reagent is discussed.

At the end of each experiment the soil was allowed to cool in the reactor. The cooled soil was removed into a clean glass jar, sealed and tumbled on a roller mill. A 2 to 3 g sample of soil was taken and placed in a preweighed thimble. Approximately, 6 to 7 g of anhydrous sodium sulfate was mixed in with the soil. The mixture was set aside for two hours. After waiting for two hours, the thimble was transferred to a Soxhlet extraction apparatus. Approximately 150 ml of hexane was added to the flask and the soil extracted for a period of 16 hr with continuous reflux of the condensed solvent phase. After extraction, the solvent was removed and blown down to approximately 1 to 3 ml with nitrogen and gentle heating. The volume of the concentrated extract was brought up to 10 ml in a volumetric flask. The prepared solution was analyzed for Aroclor 1242 on a gas chromatograph equipped with an electron capture detector.

LIQUID-LIQUID EXTRACTION OF CONDENSATE

Vaporized water and other gases formed during the thermal decontamination experiments were conveyed to a cold trap where the moisture was condensed. The water was recovered at the end of each experiment and weighed. Typically two traps were used in every experiment. The water from each trap was extracted in a separatory funnel by mixing it with hexane and shaking the funnel on a wrist action shaker. After separation of the hexane phase from the funnel, the water phase was extracted twice more for a total of three times. All the hexane extracts from both the traps were combined and blown down according to the procedure described in the previous sub-section. The concentrated extract was analyzed on a GC/ECD system.

GC ANALYSIS OF THE EXTRACT PHASE FOR AROCLOR 1242

The analysis is performed on a Hewlett-Packard 5840A gas chromatograph equipped with a Ni^{63} electron capture detector and a 6 ft. x .25 in. ID silanized glass column packed with 3% SP2250 on 100/120 mesh Supelcoport. The GC operating parameters are: injector temperature 300°C; detector temperature 325°C, carrier gas (5% methane/95% argon) flow rate of 60 ml/min; column temperature isothermal for the first 40 minutes at 180°C, followed by a 30°C/min ramp to 240°C, where it was maintained for a period of 10 minutes. The purpose of the ramp was to condition the column for the next injection.

The extract phase stored in 10 ml volumetric flasks at -20°C was allowed to warm up to room temperature prior to GC analysis. After warming and checking the volume integrity, an aliquot of 2 µl of the sample was injected using the solvent flush method (2 µl air, 2 µl HPLC grade hexane, 2 µl sample, 1 µl air). The area sum of all peaks eluting in the time interval of 1.8 to 44.0 minutes was calculated and used for data reduction. The determined area was compared to a calibration curve based on 1-100 ng/µl of Aroclor 1242 in iso-octane. If the peak area exceeded the range of the calibration curve then the samples were diluted and re-injected.

GC CALIBRATION PROCEDURE

The GC system was calibrated using the external standardization techniques. Calibration standards were prepared from Aroclor 1242 at six levels by dilution in iso-octane. For the purpose of making calibration standards, 1.0 µg/µl standard solution in iso-octane was purchased. This was diluted to 1, 10, 25, 50, 75 and 100 ng/µl in iso-octane. Blank solvent was also injected to verify zero response on the GC.

A full calibration curve is shown in Figure B-1. A linear regression line is shown on the figure together with the 95% confidence band. Calibration standards were run daily and the results compared with the full calibration curve. The daily runs of the standards were done to bracket the concentrations of the unknown samples analyzed on that day.

EXTRACTION EFFICIENCY

The extraction efficiency was determined at three different concentrations of Aroclor 1242 in sandy soil used in the thermal decontamination experiments. Spiked samples of soil were extracted by the Soxhlet extraction procedure and the prepared extract was analyzed by the GC/ECD system to determine the recovery efficiency. The soil was spiked by a preanalysed solution of Aroclor 1242 in iso-octane. The spiked soil was placed in a glass jar and tumbled on a roller for a period of two to four hours to homogenize the soil with the spike.

The data for extraction efficiency is presented in Figure B-2, which is a box-plot of recovery efficiency vs soil concentration level in the range of 208 to 1075 ppm. The horizontal line drawn through the box indicates the median recovery efficiency, the upper and lower sides of the box represent the inter-quartile range of the observed extraction efficiency. The two tails attached to each box indicate the observed range of the data. The apparent concentration of Aroclor 1242 for each unknown sample was corrected by the recovery efficiency to determine the true concentration.

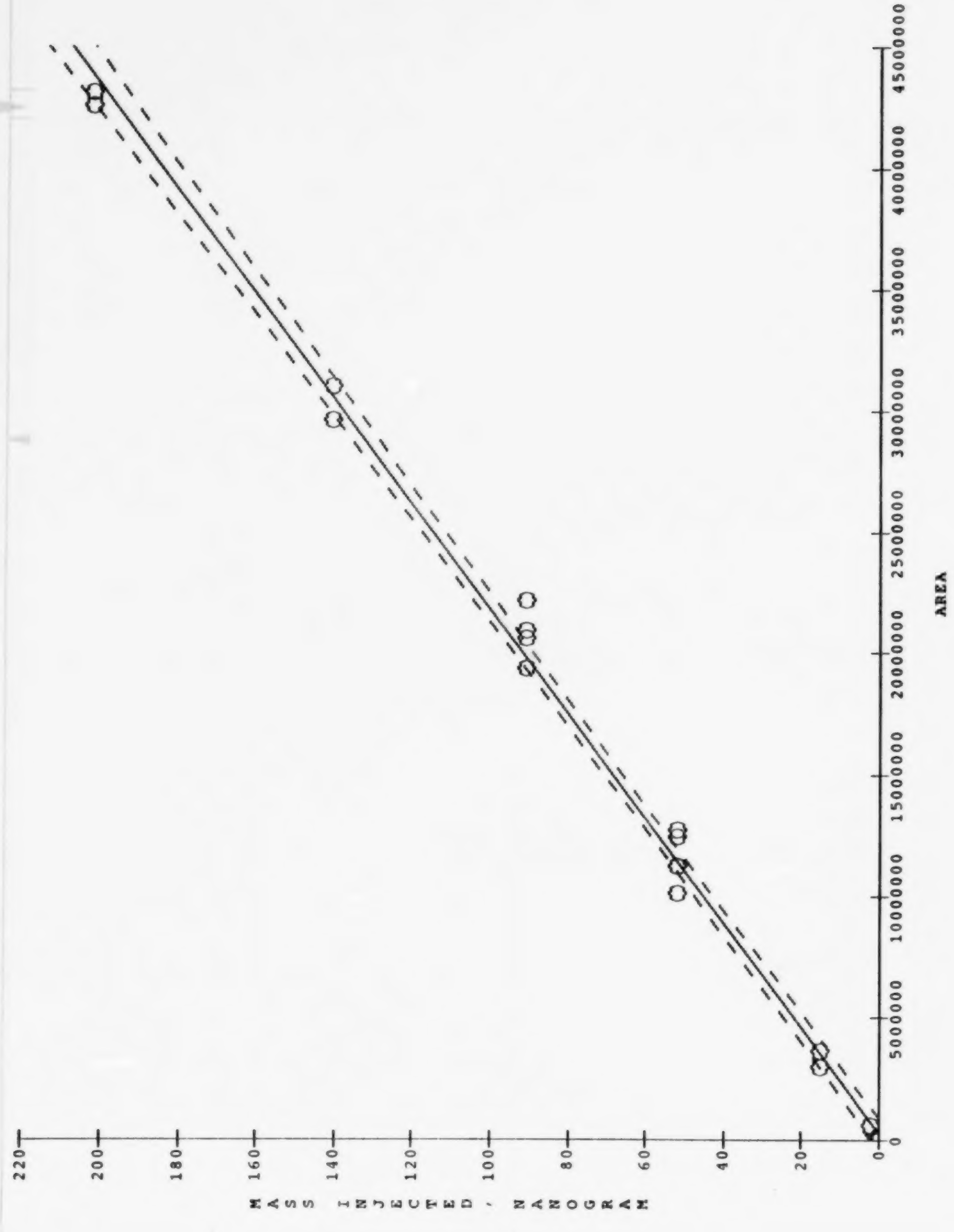
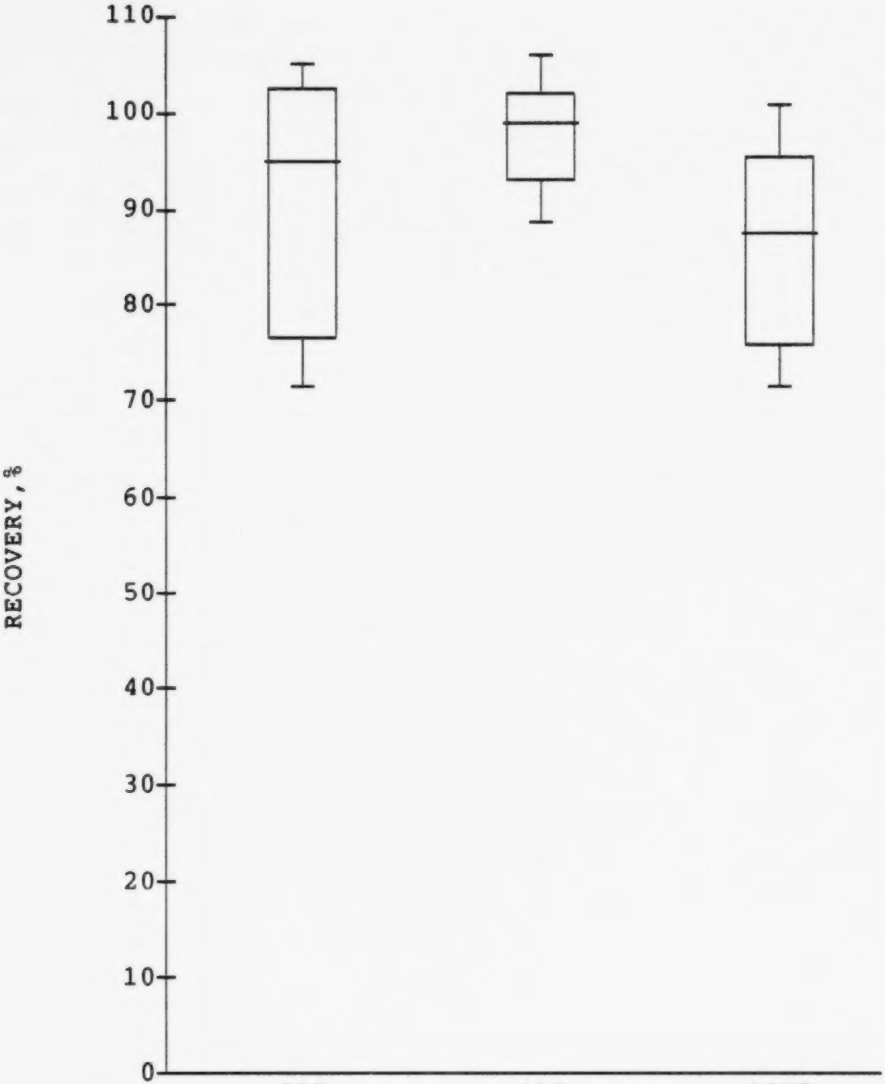


Figure B-1. Calibration curve for Aroclor 1242.



CONCENTRATION,PPM	208	416	1075
# Pts	11	11	8
Mean	92.081818	98.481818	86.2625
IQR	26	8.9	19.7

Figure B-2. Recovery efficiency for Aroclor 1242.

CALCULATION OF AROCLOR 1242 CONCENTRATION IN SOIL

As discussed earlier, the area sum of all the peaks in the time interval of 1.8 to 44.0 minutes was compared against the calibration curve to obtain the concentration of the prepared extract. For soil samples the equivalent concentration in soil was calculated by the following equation:

$$C = \frac{\frac{R_x}{R_s} \cdot C_s \cdot 10^4}{W_s} (X_r)^{-1}$$

$$R_x = \frac{A_x}{V_x}$$

$$R_s = \frac{A_s}{V_s}$$

where A_x = area of unknown sample peaks
V_x = injection volume of sample (µl)
A_s = area of standard peaks
V_s = injection volume of standard (µl)
C_s = concentration of standard (µg/µl)
10^4 = µl/10 ml of sample solution
W_s = weight of soil extracted (g)
X_r = extraction efficiency

APPENDIX C

PROCEDURE FOR ANALYSIS OF SOIL FOR AROCLOR 1260

A procedure for soil extraction, extract phase cleanup and analysis of the extract phase for Aroclor 1260 was developed and verified. The main reason for the time taken to verify the procedure was due to the presence of polyethylene glycol in the soil matrix. Therefore, it was necessary to verify all three steps in order to ensure that there were no interferences by the PEG during any one of the three steps involved. Polyethylene glycol is left behind in the soil after the reaction is quenched by the addition of hydrochloric acid to the soil. The acid neutralizes any remaining unreacted KPEG to form PEG and KCl. The procedure for the analysis is described in this Appendix.

SOIL SAMPLE EXTRACTION AND CLEANUP

The procedure described below is for the analysis of Aroclor 1260 contaminated soil containing potassium polyethylene glycolate (KPEG). This procedure was followed after conducting experiments in which contaminated soil was treated with KPEG at high temperature, up to 140°C.

The soil containing Aroclor 1260 and KPEG was removed from the reactor and placed in a crystallizing dish containing a known quantity of chilled 0.1N hydrochloric acid. The acid was used to neutralize the excess KPEG present in the soil. This was done to stop the reaction between KPEG and the PCBs. The soil and HCl were thoroughly mixed and the pH of the slurry was checked with a pH paper. Additional acid was added if necessary to adjust the pH to approximately 6.0.

The crystallizer dish containing the soil and HCl was weighed and then placed in an oven at 110°C for a period of at least 18 hrs. to boil-off the moisture. At the end of this period the dish was removed from the oven and cooled in a desiccator. The weight of the cooled dish and soil was recorded and then the entire quantity of soil was transferred to an amber glass jar with a Teflon®-lined screw cap. This jar was tumbled for 2 hours to ensure homogeneity.

A 5 to 7 gm portion of the soil was weighed in a beaker to the nearest 0.1 gm. A quantity representing 30% by weight of soil of anhydrous sodium sulfate was added to the soil in the beaker, mixed, and allowed to stand for 2 hours. At the end of 2 hours the mixture was remixed in the beaker and allowed to stand for another 2 hours. After approximately 4 hours, the mixture was transferred to a cellulose extraction thimble and extracted for 16 hours with 150 ml of pesticide grade n-hexane in a Soxhlet extractor.

The extract was washed two times with 50 ml of Na_2SO_4 saturated deionized water. The washed extract and all rinses were collected in a 250 ml round bottom flask, approximately 3 ml of pesticide grade isooctane was added and the solution was blown down to approximately 1 to 3 ml volume with gentle heating (~ 40°C water bath) under a nitrogen stream. The concentrate and rinses were transferred to a 10 ml volumetric flask through a tightly packed glass wool plug and brought to volume with n-hexane. One to two drops of triple-distilled mercury were added and the flask was vigorously shaken for 30 seconds. The solution was then stored at -20°C until analysis. (Occassionally a small amount of water was visible in the concentration step; this was removed by adding pesticide grade MeOH until one phase remained, then continued with the concentration step.)

GC ANALYSIS OF THE EXTRACT PHASE FOR PCBs

The analysis was performed on a Hewlett-Packard 5840A gas chromatograph equipped with a Ni^{63} electron capture detector and a 2 meter x 2 mm ID silanized glass column packed with 3% SP2100 on 100/120 mesh Suplecoport. The GC operating parameters are: injector temperature, 300°C; detector temperature, 300°C; carrier-gas (5% methane/95% argon) flow rate of 60 ml/min; column temperature, 200-215°C (isothermal).

The extract phase stored in 10 ml volumetric flasks at -20°C was allowed to warm up to room temperature prior to GC analysis. After warming and checking the solution volume integrity, an aliquot of 1 to 2 µl, measured to the nearest 0.05 µl was withdrawn with a 10 µl syringe. The solvent flush method (2 µl air, 1 µl isooctane, 1 µl air, sample, 1 µl air) was used. Determined GC area responses were corrected to a 2 µl injection. The sum of five peaks in the chromatogram, containing approximately 40% of the total PCB area was used to determine the area response. These five peaks are shown in Figure C-1, which is a chromatogram of PCB 1260 standard solution in isooctane. The determined area was compared to a calibration curve based on 2.5 to 500 ng/µl of Aroclor 1260 in isooctane. If the peak areas exceeded the linear range of the system, then the sample extracts were diluted and reanalyzed.

GC CALIBRATION PROCEDURE

The GC system is calibrated using external standardization techniques. Calibration standards are prepared from Aroclor 1260 at five suitable concentration levels by dilutions in isooctane. For the purpose of making calibration standards, 1000 ppm Aroclor 1260 standard solution in isooctane were purchased. These were diluted to 250, 150, 100 and 25 and 2.5 ppm in pesticide grade isooctane. Additional standards at 10 and 75 ppm were prepared later. Blank isooctane samples were also injected to verify zero response on the GC. A GC calibration curve was generated by injecting the prepared calibration standards. The calibration standards are stored in glass vials having a screw cap fitted with a teflon liner. When the samples are first prepared, the liquid level in each vial is marked to check for evaporation losses, etc. When the standards are not in use they are stored at -20°C. Prior to use, each standard is allowed to warm up to room temperature and the liquid level verified.

A full calibration curve is shown in Figure C-2. In this curve the sum of the peak area response for the 5 peaks identified in Figure C-1 is plotted against the Aroclor 1260 concentration of the standard.

A two-point GC calibration was verified daily. If the daily check of the calibration curve indicates a deviation of more than 10%, then a new calibration curve containing 4 or 5 points was generated. To further ensure reliable GC analysis of samples, calibration standards are run each day to

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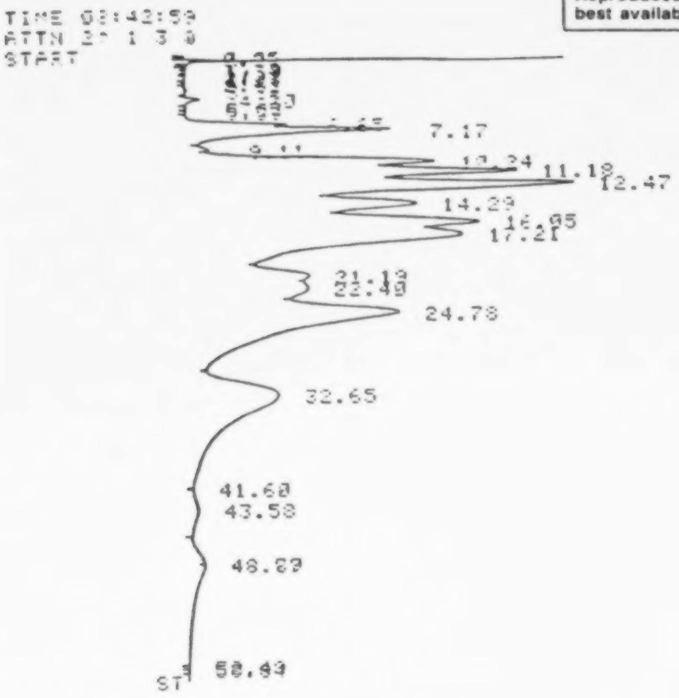

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HP RUN # 164          MAR/06/85        TIME 08:47:00
AREA %

   RT             AREA        AREA %

  0.38         3862000         1.135
  4.20          493100         0.145
  6.65         3198000         0.940
  7.17        12690000         3.730
  9.11         1125000         0.331
 10.24        17490000         5.141
 11.18        24640000         7.243
 12.47        37500000        11.024
 14.29        25760000         7.572
 16.05        28400000         8.348
 17.21        48620000        14.292
 21.19        14280000         4.198
 22.40        17200000         5.056
 24.78        55960000        16.450
 32.65        38000000        11.171
 43.58         3602000         1.059
 48.79         2479000         0.729
 48.87         4882000         1.435

DIL FACTOR: 1.0000 E+ 0
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Figure C-1. Chromatogram of standard solution of Aroclor 1260 at 100 ng/µl.

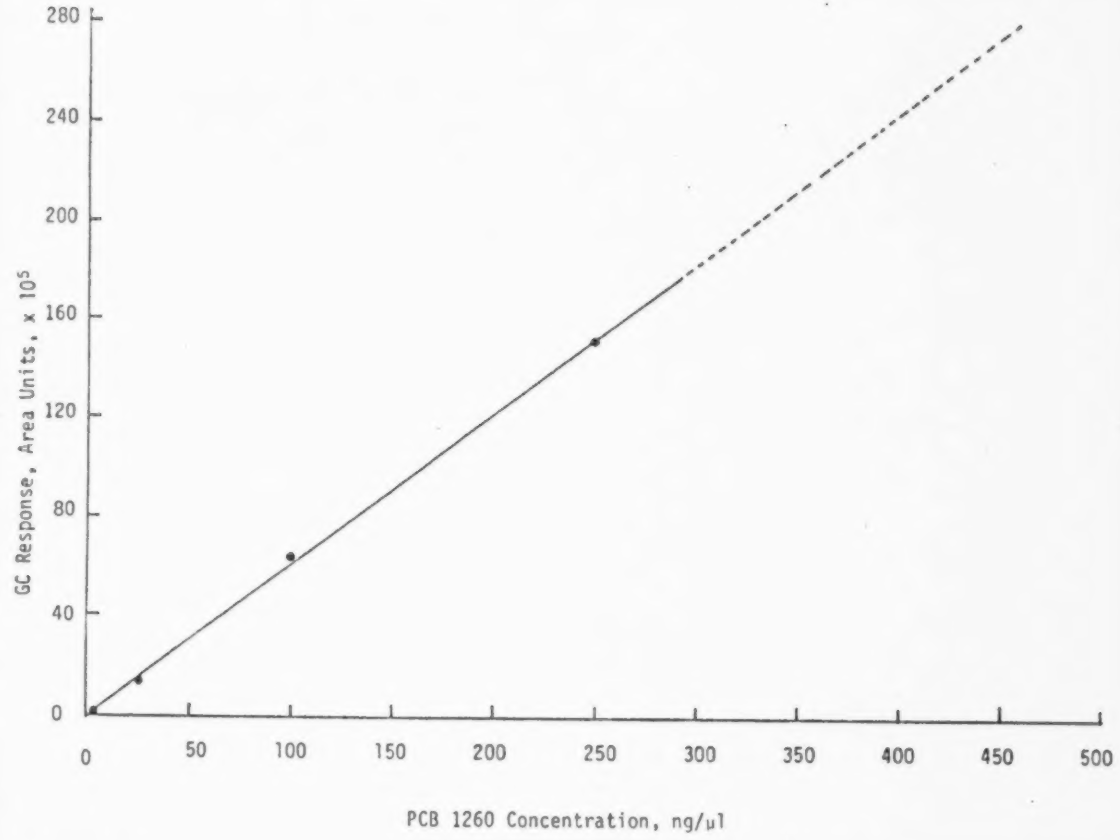

Figure C-2. GC calibration curve for Aroclor 1260.

bracket the concentration of the samples. For example, if the samples were analyzed to contain 200 ppm Aroclor 1260, then calibration standards were run at 250 and 150 ppm to bracket the sample.

Fresh calibration standards were prepared every 10 working days or when a volume loss exceeding 5% is observed in the calibration standard storage vials.

AROCLOR 1260 EXTRACTION EFFICIENCY

The extraction efficiency was determined as a function of Aroclor 1260 concentration in soil. Spiked samples of soil were prepared at several different concentration levels. The soil was spiked with a solution of Aroclor 1260 in acetone and homogenized. The concentration of Aroclor 1260 in this solution was determined and the volume necessary for achieving the desired concentration was added to the soil. The spiked soil was placed in a jar and tumbled for 24 hours prior to extraction and analysis. The extraction efficiency was found to be a function of concentration. The percent recovery is plotted as a function of soil concentration in Figure C-3. A straight line was fitted to the data. The regression equation fitted to the data by the method of least squares is also shown in Figure C-3. A second extraction, by the same procedure, of previously extracted soil confirmed that all extractable material was removed in the initial extraction. The extraction efficiency was used to correct the data when treated soil samples were analyzed.

The data of Figure C-3 is also shown in Table C-1. This table gives the details for the number of times each spiked soil sample was extracted and the number of times the same extract was analyzed.

The soil sample labeled A through D were also sent to an independent laboratory for analysis. This was done to explore ways to expedite the progress on other tasks. The results are shown in Table C-2. Based on these results it was decided to perform all analytical work in-house.

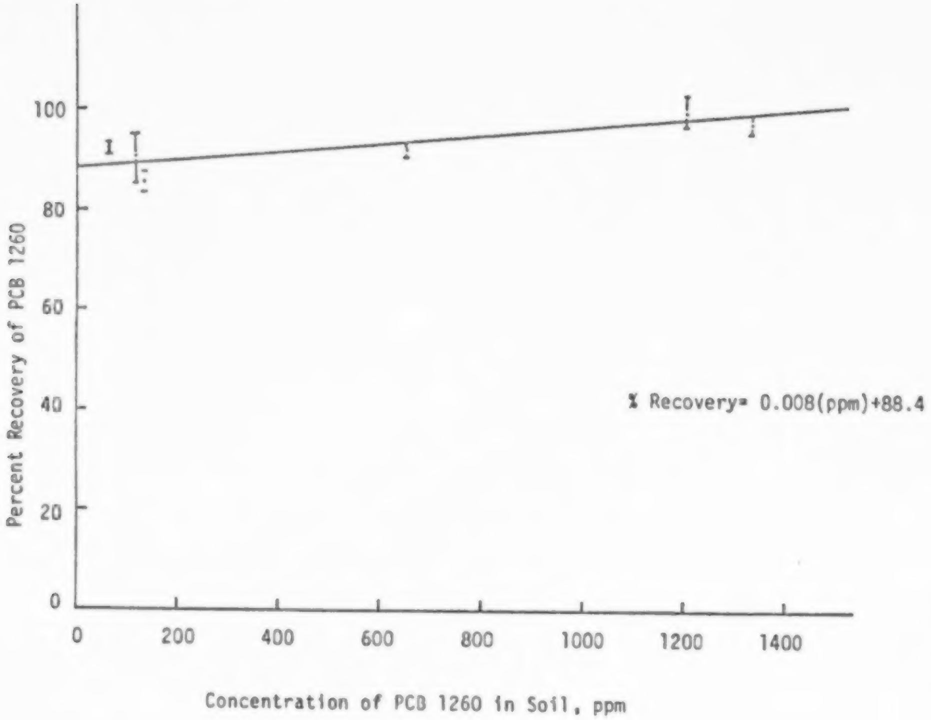

Figure C-3. Percent recovery vs. true concentration of Aroclor 1260 in soil.

TABLE C-1. DATA ON EXTRACTION EFFICIENCY FOR PCB CONTAMINATED SOIL

No. of Times Extracted	No. of Times Analyzed on GC	Soil I.D.	A	B	C	D	E	F
		Conc. Level PCB, ppm	1340	134	1210	121	65.5	655
		Conc. Level PEG 400	0	0	10%	10%	0	0
First Extraction	one		97.7%	79.1	104.1	81.9	91.5	93.4
	two		-	-	-	-	93.1	91.5
2nd Extraction	one		101.7%	85.3	60.3[2]	69.1[3]	-	-
	two		98.3%	-	-	-	-	-
3rd Extraction	one		75.8%[1]	85.4	94.2	84.5	-	-
4th Extraction	one		90.2%	86.0	96.3	101.6	-	-
	two		-	90.1	-	93.4	-	-
5th Extraction	one		101.5	-	105.1	-	-	-
	two		94.8					
	three		98.3					
	Average		97.5	85.2	99.9	90.4	92.3	92.5
	S.D.		4.0	3.9	5.5	9.0		
	n		7	5	4	4	2	2

[1] Not included in average.

[2] Not included in average, extracted for only 4 hours.

[3] Not included in average, Soxhlet ran dry.

TABLE C-2. COMPARISON OF PCB ANALYSIS IN SOIL PERFORMED BY IITRI AND OUTSIDE INDEPENDENT LAB

Sample ID	True PCB Conc. ppm	Percent Recovery of Aroclor 1260		Remarks
		IITRI*	Outside Lab.	
A	1340	97.5	95.5	
B	134	85.2	27.6	
C	1210	99.9	58.7	PEG added
D	121	90.4	43.0	PEG added

* Values are averaged over several extractions and GC analyses.

CALCULATION OF PCB CONCENTRATION IN SOIL

As discussed earlier, five peaks were identified in the PCB chromatogram such that the sum of their area response was linear with PCB concentration over a range of 2.5 to 250 ng/µl. These five peaks were obtained from an analysis of standard PCB solution. For the purpose of analyzing for Aroclor 1260 in soil, all calculations were based on the sum of the areas of the same five peaks. The concentration of PCB in the soil was determined by the following equation.

$$\text{concentration in soil} \quad L_o = \frac{\frac{R_x}{R_s} \cdot C_s \cdot 10^4}{W_s} (\eta_R)^{-1} \left(\frac{W_o}{W_i}\right) \qquad (1)$$

$$R_x = \frac{A_x}{V_x}$$

$$R_s = \frac{A_s}{V_s}$$

where
A_x = area of unknown sample peaks
V_x = injection volume of sample (µl)
A_s = area of standard peaks
V_s = injection volume of standard (µl)
C_s = concentration of standard (ng/µl)

10^4 = µl/10 ml of sample solution

W_s = weight of soil extracted (g)

W_o = weight of soil after reaction, neutralization, and drying

W_i = initial weight of soil added to reactor

η_R = extraction efficiency

In equation (1) above, η_R is the extraction efficiency correction applied to the determined concentration to obtain the true concentration. The term (W_o/W_i) is a correction applied to report the data on a KPEG free basis in order to make the PCB concentration comparable to the initial untreated soil sample. The ratio (W_o/W_i) is greater than 1.0 because of excess KPEG and neutralization reaction products which are present in the treated soil.